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Gaseous HCl and Chlorinated Organic Compound Emissions from Refuse Fired Waste-to-Energy Systems

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GASEOUS HCl AND CHLORINATED ORGANIC COMPOUND EMISSIONS FROM REFUSE FIRED WASTE-TO-ENERGY SYSTEMS

by

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16. ABSTRACT

The emissions from a water wall mass fired municipal waste incinerator and a refuse derived fuel (RDF) fired incinerator were sampled for chlorinated organic compounds and hydrochloric acid (HCl). The sampling was performed to evaluate the extractive sampling methods used to measure the compounds.

Sampling the chlorinated organic compound emissions was conducted using a modified version of the EPA Reference 5 Method, which included an XAD-2 resin cartridge. HCl was sampled with an impinger train using basic absorbing solutions.

The recovered chlorinated organics were separated into chlorophenols, chlorobenzenes, poly-chlorinated biphenyls (PCBs), chlorinated dibenzo-p-dioxins (CDDs), and chlorinated dibenzofurans (CDFs), and quantitated.

The results of the analysis are prsented in terms of the compounds distributions' within the sampling systems as well as the emission rates.

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ABSTRACT

Testing of the emissions of hydrogen chloride (HCl), chlorinated dibenzo-p-dioxins, dibenzofurans, chlorobenzenes, chlorophenols, polychlorinated biphenyls, and aldehydes was conducted on a water wall mass fired municipal waste incinerator and a refuse derived fuel (RDF) fired municipal waste incinerator. The purpose of the testing was to evaluate the measurement methods used for sampling and to determine what differences may exist in the emission characteristics of the two types of units and the effect that this difference would have on the applicability of the methods employed.

Testing of HCl emissions was performed by absorption in four midget impingers each containing 20 ml of 0.1 N NaOH. Testing at the RDF fired incinerator included parallel sampling with an EPA Method 5 train with 100 ml of 0.1 N NaOH in each of the first two impingers.

Sampling of chlorinated organic compound emissions was conducted using a modified EPA Method 5 sampling train with a cartridge of XAD-2 resin between the third and fourth impingers. Analysis was performed using high resolution gas chromatography/mass spectroscopy.

HCl emissions from the mass fired incinerator (Site A) exceeded the HCl emissions from the RDF fired incinerator (Site B) by approximately 45%. Chlorinated organic compound emissions from Site A exceeded those from Site B by factors ranging from 12 to 371. Emissions from both sources exhibited a large variation from test to test however, isomeric distributions were similar.

The majority of all organic compounds were detected in the back half of the Method 5 sample train with the largest overall percentage found in the impinger contents. Chlorobenzenes were the only compounds of which the majority were detected in the XAD-2 resin trap.

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LIST OF ABBREVIATIONS

CPs -- chlorophenols
CDDs -- chlorinated dibenzo-p-dioxins
CDFs -- chlorinated dibenzofurans
ClBs -- chlorobenzenes
PCBs -- polychlorinated biphenyls
TrCPs -- trichlorophenols - $C_6H_2Cl_3OH$
TeCPs -- tetrachlorophenols - C_6HCl_4OH
P_5CP -- pentachlorophenol - C_6Cl_5OH
TCDDs -- tetrachlorinated dibenzo-p-dioxins - $C_{12}O_2H_4Cl_4$
PCDDs -- pentachlorinated dibenzo-p-dioxins - $C_{12}O_2H_3Cl_5$
HxCDDs -- hexachlorinated dibenzo-p-dioxins - $C_{12}O_2H_2Cl_6$
HpCDDs -- heptachlorinated dibenzo-p-dioxins - $C_{12}O_2HCl_7$
OCDD -- octachlorinated dibenzo-p-dioxin - $C_{12}O_2Cl_8$
TCDFs -- tetrachlorinated dibenzofurans - $C_{12}OH_4Cl_4$
PCDFs -- pentachlorinated dibenzofurans - $C_{12}OH_3Cl_5$
HxCDFs -- hexachlorinated dibenzofurans - $C_{12}OH_2Cl_6$
HpCDFs -- heptachlorinated dibenzofurans - $C_{12}OHCl_7$
OCDF -- octachlorinated dibenzofuran - $C_{12}OCl_8$
CDlBs -- dichlorobenzenes - $C_6H_4Cl_2$
TrClBs -- trichlorobenzenes - $C_6H_3Cl_3$
TeClBs -- tetrachlorobenzenes - $C_6H_2Cl_4$
P_5ClBs -- pentachlorobenzenes - C_6HCl_5
HxClB -- hexachlorobenzene - C_6Cl_6
TrCBs -- trichlorinated biphenyls - $C_{12}H_7Cl_3$
TeCBs -- tetrachlorinated biphenyls - $C_{12}H_6Cl_4$
P_5CBs -- pentachlorinated biphenyls - $C_{12}H_5Cl_5$
HxCBs -- hexachlorinated biphenyls - $C_{12}H_4Cl_6$

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SECTION I

INTRODUCTION

Subsequent to reports in the late 1970's that various incineration processes give rise to emissions of chlorinated dibenzo-p-dioxins (CDDs) and chlorinated dibenzofurans (CDFs), the United States Environmental Protection Agency conducted preliminary investigations of a resource recovery incenerator which further indicated the presence of these compounds. The results of this program which included data of a qualitative rather than quantitative nature, indicated the need for further investigation of the sampling methods used and, as a result, the present program was embarked upon in early 1981.

The purpose of this program was to evaluate measurement methods used for sampling chlorinated hydrocarbons, gaseous hydrochloric acid (HCl) and particulate chloride. Chlorinated hydrocarbons, HCL and particulate chlorides were collected with extractive sampling systems. Sampling was performed at a water wall mass fired and a refuse derived fuel (RDF) fired municipal waste incinerators. Initial plans to evaluate a prototype HCl monitor, under development for the EPA, did not materialize since the instrument was not completed.

For the chlorinated hydrocarbons, emphasis was placed on the distribution of specific compounds and compound classes in the sampling system. Chlorobenzenes and chlorophenols were determined, as well as the CDDs, CDFs and polychlorinated biphenyls (PCBs), since they had been implicated as precursors to the formation of the latter compounds in the combustion process. The purpose of testing the two different types of incinerators was to determine the variation of the compound-distribution in the sampling system as a function of incinerator type and particulate loading. Water wall mass fired and RDF fired incinerators were chosen for the program because they are the most prevalent types of waste to energy systems currently in operation or likely to become operational in the near future.

In addition to the chlorinated organic compounds, sampling and analysis was conducted for HCl emissions from the two units using two common sampling and analysis approaches. This was conducted in order to evaluate the distribution in the gas stream of the chlorides released from the refuse during the combustion process, and the applicability of the manual method.

SECTION 2

SUMMARY AND CONCLUSIONS

The testing conducted on the two systems revealed considerable diffences in the emission characteristics of the mass fired water wall incinerator and the RDF fired incinerator with the emissions from the mass fired unit higher in all cases. A summary of the emissions from each unit tested is presented in Table 1. Presented also are the Relative Standard Deviations for each class of compounds. This shows the varibility of emissions over time.

HCl emissions (based on the g HCl/Kg of material burned) from the mass fired incinerator (Site A) exceeded the HCl emissions from the RDF fired incinerator (Site B) by approximately 45%. Chlorinated organic compound emissions from Site A exceeded those from Site B however, by factors ranging from 12 to 371. The overall distribution of chlorides in the gas streams, which is presented in Table 2. shows that a higher percentage of total chlorides was emitted as HCl from Site B than from Site A thus indicating that combustion was more efficient for the RDF fired incinerator. This difference may be due to differing moisture contents of the two types of fuel. The RDF was stored in silos and was never exposed to moisture thus it was very dry when combusted. the fuel for Site A, on the other hand, was often quite wet as it was stored in open areas where it was exposed to rainfall.

TABLE 1. SUMMARY OF EMISSIONS DATA

Compound	Site A Emission Rate* (mg/hr)	Site A RSD** (%)	Site B Emission Rate (mg/hr)	Site B RSD** (%)
HCl	6.1	71%(17)	7.6	97%(11)
T_eCDD	15.3	72%(3)	0.1	117%(3)
P_5CDD	19.7	79%(3)	0.1	119%(3)
H_xCDD	31.5	87%(3)	0.2	99%(3)
H_pCDD	35.4	84%(3)	1.5	75%(3)
OCDD	9.2	69%(3)	0.8	62%(3)
T_eCDF	76.5	73%(3)	1.3	69%(3)
P_5CDF	35.0	72%(3)	0.5	89%(3)
H_xCDF	41.2	65%(3)	0.9	86%(3)
H_pCDF	36.5	88%(3)	3.2	105%(3)
OCDF	2.6	104%(3)	0.4	60%(3)
DClB	56.3	139%(3)	0.3	121%(3)
T_rClB	228.0	153%(3)	5.8	102%(3)
T_eClB	355.0	144%(3)	8.0	120%(3)
P_5ClB	551.0	195%(3)	39.9	169%(3)
H_xClB	165.0	110%(3)	21.6	154%(3)
T_rCP	2,444.0	78%(3)	149.0	77%(3)
T_eCP	1,127.0	88%(3)	215.0	45%(3)
P_5CP	588.0	113%(3)	352.0	94%(3)
T_rCB	14.6	125%(2)	--	--
T_eCB	8.4	99%(2)	--	--
P_5CB	1.7	90%(2)	--	--
H_xCB	0.9	125%(2)	--	--
Aldehydes	166.0	177%(2)	9.4	89%(3)

*Average of all tests at each site, HCl in Kg/hr

**RSD - Relative Standard Deviation, (number of determinations)

TABLE 2. CHLORIDE DISTRIBUTION IN GAS STREAM

Compounds	Percent of Total Chlorides in Gas Stream (%) Site A	Site B
HCl	99.92237	99.992178
Chlorophenols	0.05233	0.007650
Chlorobenzenes	0.02136	0.000079
Chlorinated Dibenzofurans	0.00235	0.000064
Chlorinated Dibenzo-p-Dioxins	0.00140	0.000029
Polychlorinated Biphenyls	0.00019	0.000000
	100.0	100.0

SECTION 3

SITE DESCRIPTIONS

As stated in Section 1, this program consisted of tests conducted at two separate facilities. The first facility, Site "A", is a mass fired, water wall, refuse burning incinerator-boiler which is used to generate steam for various purposes at a nearby research center. The unit burns 100% refuse with no auxiliary fuel at a rate of approximately 90,000 to 135,000 kg per day (100 to 150 tons/day). The unit is operated at or near capacity at all times except when firing excessively wet trash.

Site "A" was tested on September 14, 15, 21 and 22, 1981. Testing was conducted in a 1.2 meter diameter duct downstream of an electrostatic precipitator.

The second facility which was tested, Site "B", is a Detroit Rotograte Stoker Boiler which produces steam for plant heating. The unit is designed to burn coal, on which it is usually fired. The facility operators are, however, investigating the possibility of switching to RDF as a fuel and the boiler was fired on 100% RDF during testing. During testing, Site "B" was fired at a rate of approximately 205 Mg (225 tons) of RDF per day. In order to conserve fuel, the boiler was co-fired with coal during the night when testing was not conducted. Prior to the start of testing the next day, however, approximately two hours was allowed for all coal to pass through the boiler and for the unit to resume operation on 100% RDF.

Site "B" was tested on June 17 and 18, 1982. Testing was conducted in a rectangular duct at a point downstream of an electrostatic precipitator but prior to the common duct and stack used by all boilers in the heating plant.

SECTION 4

SAMPLING AND ANALYTICAL PROCEDURES

Presented in this section are descriptions of the sampling and analytical procedures which were used during this project.

SAMPLING METHODS

HCl Sampling

Sampling for HCl concentrations in the exhaust stream was conducted by two methods. The first method, which was used at both sites, involved pulling a sample through a stainless steel probe, through four midget impingers each containing 20 ml of 0.1 N NaOH, through a diaphragm pump and finally through a flow meter, flow control valve, and a dry gas meter. This sampling configuration is presented in Figure 1.

The sample was drawn at a rate of approximately 2 liters per minute and sampling was conducted for 30 minutes, thus a sample volume of approximately 0.06 m^3 was collected. The impingers containing the absorbing solution were submerged in an ice bath during sampling. Following sampling, the impinger contents were placed in labelled sample jars where they were maintained until analyzed on site.

The other sampling method which was used at Site "B" was a direct adaptation of EPA Method 5 with the only modification being that 100 ml of 0.1 N NaOH was placed in the first two impingers rather than water. The purpose of operating this train was to evaluate it in comparison to the primary method discussed above. Ideally, a complete evaluation would have involved a complete isokinetic traverse of the stack utilizing normal Method 5 procedures. It was not possible to do so in this case however, due to the limited amount of time that the boiler could be operated under test conditions. As a result, a one point sample was collected from the same area in the stack and at the same time that sampling was conducted by the primary method. This allowed both samples to be collected from the same gas stream thus providing directly comparable results with differences attributable only to the differences in the sampling methodologies.

Samples were collected for 30 minutes by this method with a sample volume of approximately 0.4 m^3 collected. After sampling, the impinger contents were placed in labelled sample jars where they were maintained until being analyzed on site. The filter and probe wash were placed in with the impinger contents.

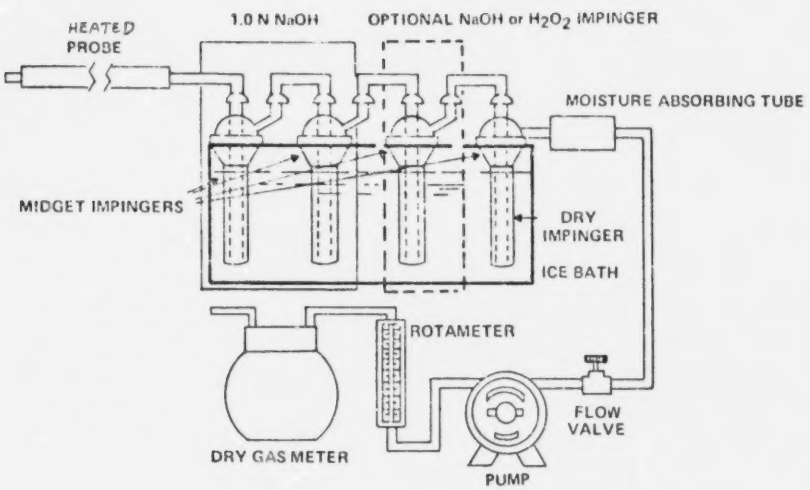

FIGURE 1. GASEOUS HCL SAMPLING TRAIN

Organic Compound Sampling

Organic compound sampling was conducted using a modified EPA Method 5 sampling system. This system, as depicted in Figure 2, consisted of a heated glass lined sample probe with a stainless steel nozzle; a glass fiber filter in a heated glass filter holder with a stainless steel filter support; a Greenburg-Smith impinger containing 100 ml distilled water followed by a modified Greenburg-Smith impinger (dry) for mist knockout, both containing 5 cm of 3-6 mm diameter glass beads and immersed in an ice bath; a resin cartridge containing 60 g of XAD-2 sorbent resin; and finally an impinger containing 200-300 g of silica gel. Sample flow was measured and controlled by a conventional EPA Method 5 meter box. All glassware used in the tests was annealed prior to being taken into the field.

Sampling was conducted isokinetically during all tests. Tests were conducted for 180 and 300 minute time periods with sample volumes ranging from 2.5 to 6.8 m^3.

After each test, great care was taken in the recovery of samples. The glass fiber filter was removed from the glass filter holder along with any large particulate matter adhering to the filter holder and transferred to a sealed glass container. Particulate matter and any condensate was recovered from the probe nozzle, probe fitting, probe liner, and front half of the filter holder by repeatedly brushing and rinsing these components with HPLC Grade Toluene and placing the wash in a sealed glass container with a Teflon lined cap. This procedure was repeated with HPLC Grade Methanol with the washings being placed in a separate sealed glass container with a Teflon lined cap.

The contents of impingers #1 and #2 were recovered, measured, and placed in a sealed glass container with a Teflon lined cap. These impingers and all connecting glassware downstream of the filter including the back half of the filter holder were rinsed with HPLC Grade Toluene and the washings were added to the recovered impinger solution. This procedure was repeated with HPLC Grade Methanol with the washings placed in a separate sealed glass container with a Teflon lined cap.

The XAD-2 resin was left in its glass cartridge. Glass caps were placed on the ends of the cartridge.

The contents of the silica gel impinger were transferred to its original sealed container for subsequent weighing. The silica gel was used only for the determination of stack gas moisture content.

Additional Parameters

The additional gas stream parameters which were sampled along with the organics sampling included temperature, moisture content, velocity, volumetric flow rate, and molecular weight. These parameters were sampled using the following EPA Test Methods:

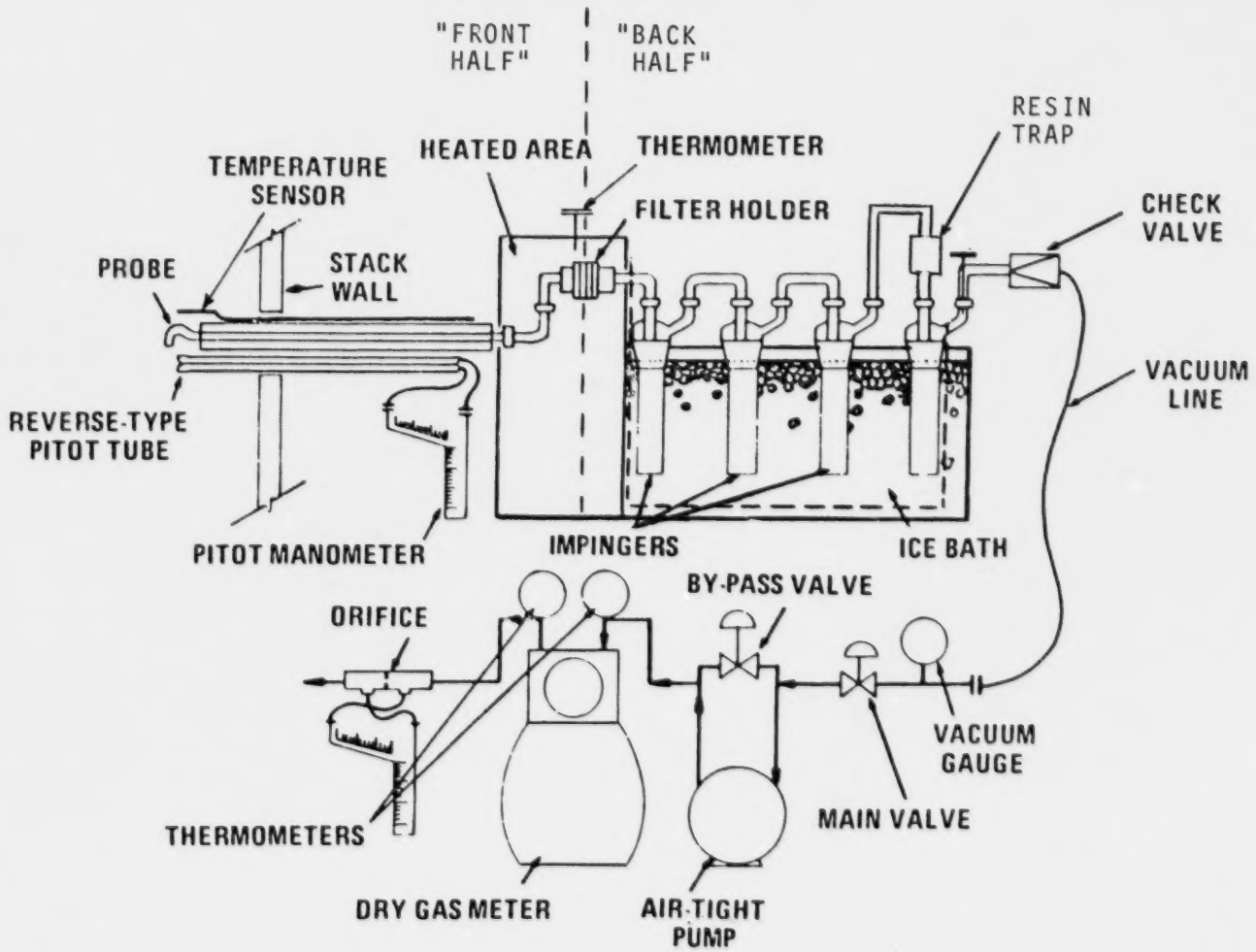

Figure 2. Organic compound sampling system.

Method 1 - Sample and Velocity Traverses for Stationary Sources;

Method 2 - Determination of Stack Gas Velocity and Volumetric Flow Rate;

Method 3 - Gas Analysis for Carbon Dioxide, Oxygen, Excess Air, and Dry Molecular Weight, and

Method 4 - Determination of Moisture Content in Stack Gases.

ANALYTICAL PROCEDURES

HCl Analysis

HCl analysis was performed by the mercuric nitrate ($Hg(NO_3)_2$) method which involves titrating Cl^- with a standardized $Hg(NO_3)_2$ solution using a diphenylcarbazone indicator-acidifier reagent. This method is known to be subject to interference and endpoint masking by the presence of sulfite (SO_3^{2-}) and cationic metals in the exhaust stream. In order to alleviate this problem, samples were treated with 3% Hydrogen Peroxide to eliminate the sulfite interference and they were passed through a Rexyn 101-H column to eliminate the cationic endpoint masking.

The results of the analysis yielded the total milligrams of HCl in the sample. This was divided by the sample volume collected to yield the stack gas HCl concentration.

Organic Compound Analysis

Halocarbons--

The procedures used to separate the halocarbons of interest from the matrices in which they were collected involved solvent extraction with the addition of internal standards of $^{37}Cl_4$-2,3,7,8-TCDD, $^{37}Cl_7$-1,2,3,4,6,7,8-H_pCDD, $^{37}Cl_8$-OCDD, D_6-3,3',4,4'-tetrachlorobiphenyl, $^{13}C_6$-pentachlorophenol, and $^{13}Cl_6$-hexachlorobenzene to each sample. The recovery percentages for each of these internal standards are presented below:

Internal Standard	Site A Samples Recovery Efficiency (%) Range	Site A Samples Recovery Efficiency (%) Average	Site B Samples Recovery Efficiency (%) Range	Site B Samples Recovery Efficiency (%) Average
$^{37}Cl_4$-2,3,7,8-TCDD	40-100	78	60-95	77
$^{37}Cl_7$-1,2,3,4,6,7,8-H_pCDD	60-100	80	50-90	73
$^{37}Cl_8$-OCDD	50-100	73	50-85	70
D_6-3,3',4,4'-T_eCB	40-100	85	40-100	76
C_6-P_5CP	40-100	87	10-100	66
$^{13}C_6$-H_xC1B	30-100	58	50-95	73

Further sample preparation procedures included acid, water, basic, and further solvent extractions, macro-column elution, and mini-column liquid chromatography. If preliminary GC-MS screening analysis of a sample indicated the presence of potential interfering compounds or other sample matrix constituents which eluted from the GC at very long times, then additional sample clean up or fractionation was required using high performance liquid chromatography (HPLC). The HPLC used for this purpose was a Varian Model 5021 Microprocessor Controlled HPLC equipped with a CDS-111L Data System. Dual Dupont Zorbax ODS Columns (25 cm x 0.6 cm I.D.) were employed. Methanol was employed as the mobile phase in the isocratic mode. Sample preparation procedures are presented in more detail in Appendix A.

The instrumentation utilized to perform the quantitative analyses for the chlorocarbons of interest comprised a gas chromatograph-mass spectrometer-data system (GC-MS-DS) which included a Perkin Elmer Sigma III Gas Chromatograph coupled through a specially modified interface to a Kratos MS-25 Double Focussing Mass Spectrometer equipped with a Kratos DS55SM Data System. This analytical system falls in a class of analysis referred to as "high resolution gas chromatography/high resolution mass spectroscopy" (HRGC/HRMS). The gas chromatograph was equipped with a split/splitless injector and a wall-coated open-tabular fused-silica capillary column. The interface mentioned above included provision for both direct admission of the column effluent into the mass spectrometer source as well as admission of the column effluent via a single-stage, all-glass jet separator. The interface was modified in order to minimize peak broadening due to excessive dead-volume and to optimize the temperature throughout the interface. The mass spectrometer was operated in the multiple ion monitoring mode under the control of the computer-based Kratos DS55SM data system. Elaborate programs for the DS55SM data system were developed which permitted rapid, automated retuning of the mass spectrometer during analysis of a sample extract and thus 20-30 separate ion-masses were sequentially monitored during an analysis. Each of the groups of chlorocarbons of interest (CDDs/CDFs, chlorobenzenes, chlorophenols, and PCBs) were analyzed separately. The GC/MS/DS parameters specifically developed for each of these groups are discussed in detail below. A very detailed discussion of the procedures for quantitating CDDs/CDFs will be presented followed by the descriptions of analgous procedures for each of the other groups of compounds.

1. CDDs/CDFs

   The tetrachlorinated through octachlorinated dibenzo-p-dioxins (CDDs) and chlorinated dibenzofurans include 136 separate isomers (49 CDDs and 87 CDFs). Since pure standards corresponding to each of these compounds are not available in any laboratory, the approach for calibration of the GC/MS-DS system, which is considered state-of-the-art, was to utilize the available standards to obtain data which is presumed to be representative of all of the isomers in the group. Calibration of the GC-MS-DS system therefore initially entailed characterization of the standards on

hand which represented each class of isomers (the degree of chlorination, e.g. monochloro, dichloro, etc. defines the "class" of isomers) known to comprise the group of compounds being determined. In the case of the CDDs/CDFs, 210 separate isomers are possible which are distributed among 8 classes (mono through octachlorinated) of CDDs and 8 classes of CDFs. The following procedure for characterization of the isomers was developed and applied.

(i) Obtain mass spectra for each available isomer standard noting in particular the relative abundances of the m^+ and $m + 1^+$ peaks.

(ii) Determine gas chromatographic retention times for each of the isomer standards on hand.

(iii) Based upon the above data select the ion-masses which are appropriate for detecting and quantitating the isomers in the class of interest and select the gas chromatographic retention time window appropriate for all isomers in the class (i.e. the time interval during which the earliest eluting and latest eluting isomers of a particular class elute from the gas chromatographic column and enter the mass spectrometer source). This retention time window must also include the retention time for the internal standard employed in quantitating the isomers of a particular class. Since a limited number of stable isotopically-labelled internal standards are available, the following ^{37}Cl-labelled standards were selected to represent the CDDs/CDFs indicated:

CDD/CDF	^{37}Cl Standard Employed for Quantitative Determinations
TCDD/TCDF PCDD/PCDF	$^{37}Cl_4$-2,3,7,8-TCDD
HxCDD/HxCDF HpCDD/HpCDF	$^{37}Cl_4$-1,2,3,4,6,7,8-HpCDD
OCDD/OCDF	$^{37}Cl_8$-OCCD

Based upon the gas chromatographic retention time data and the mass spectral data obtained as indicated above, the detailed GC-MS-DS analytical procedure in Table 3 was developed which summarizes the time sequence utilized in the analysis of tetrachlorinated-octachlorinated CDDs/CDFs. Further details of the configuration and operational parameters for the GC-MS-DS are summarized as follows:

TABLE 3. SEQUENCE OF OPERATIONS IN GC-MS-25-DS ANALYSES OF SAMPLE EXTRACTS FOR CHLORODIBENZO-p-DIOXINS AND CHLORODIBENZOFURANS

Esapsed Time (min)	Event	GC Column Temp.	Temp. Program Rate (°C/min)	Ions Monitored By Mass Spectrometer (m/z)	Compounds Monitored
0.00	Injection, splitless	190°C	--		
1.50	Turn on split valve	180°C	--		
2.00	Begin temp program to 220°C	190°C	5°C/min		
5.00	Open column flow to Mass Spect.	205°C	5°C/min		
16.00	Start MID PROGRAM #4	220°C	--	303.902	Cl_4 furans
	Sweep = 100 ppm			205.899	Cl_4 furans
	Time on Cl_4 mass = 0.15 sec			319.897	Cl_4 dioxins
	Time on ^{37}Cl-TCDD = 0.05 sec			321.894	Cl_4 dioxins
				327.885	$^{37}Cl_4$ labelled TCDD
23.75	Stop MID PROGRAM #4	220°C	--		
24.25	Start PROGRAM #5	220°C	--		
	Sweep = 750 ppm			337.863	Cl_5 furans
	Time on penta mass = 0.2 sec			339.860	Cl_5 furans
				353.858	Cl_5 dioxins
				355.855	Cl_5 dioxins
25.00	Begin temp program to 230°C	220°C	5°C/min		
34.50	Stop MID PROGRAM #5	230°C	--		
35.00	Start MID PROGRAM #6	230°C	--	373.821	Cl_6 furans
	Sweep = 150 ppm			375.818	Cl_6 furans
	Time on each mass = 0.25 sec			389.816	Cl_6 dioxins
				391.813	Cl_6 dioxins

(Continued)

TABLE 3 (Continued)

Elapsed Time (min)	Event	GC Column Temp.	Temp. Program Rate (°C/min)	Ions Monitored By Mass Spectrometer (m/z)	Compounds Monitored
50.00	Begin temp program to 235°C		5°C/min		
53.50	Stop MID PROGRAM #6	235°C	--		
54.00	Start MID PROGRAM #7 Sweep = 750 ppm Time on each mass = 0.35 sec	235°C	--	407.782	Cl_7 furans
				409.779	Cl_7 furans
				423.777	Cl_7 dioxins
				425.774	Cl_7 dioxins
				431.765	$^{37}Cl_4$ labelled HpCDD
70.0	Stop MID PROGRAM #7				
85.00	Start MID PROGRAM #8 Sweep = 750 ppm Time on each mass = 0.50 sec	235°C	--	441.743	Cl_8 furans
				443.740	Cl_8 furans
				457.738	Cl_8 dioxins
95.00	Stop MID PROGRAM #8	235°C		459.735	Cl_8 dioxins
130.00	Return to initial temp			471.717	$^{37}Cl_8$ labelled OCCD

a. Conditions for the Gas Chromatograph

Column: 50M WCOT (OV-101) Fused Silica Capillary
Carrier Gas: Hydrogen, 30 lb. head pressure
Column Temperature: Programmed, see Table 3 for Details
Interface Temperature: 250°C
Injector: Split @ 50:1

b. Conditions for the Mass Spectrometer

Ionizing Voltage: 70 eV
Accelerating Voltage: 4 KV
Source Temperature: 250°C
Multiple Ion Monitoring Mode: See Table 3 for Details

c. Data Acquisition/Handling

The DS55SM Data System and associated peripherals were employed to acquire both analogue data (total ion current plots, specific ion current monitoring plots) and digital data (peak areas) from which the quantities of CDDs/CDFs present in the samples were calculated.

d. Construction of Calibration Curves, Quantitation

The general approach to quantitating CDDs/CDFs native (i.e. the CDDs/CDFs present in the as-received sample) to each of the samples was to determine the ratios of the intensities of the mass spectral responses obtained for ion-masses characteristic of the CDDs/CDFs native to the sample vs. the intensities of responses obtained for the internal standard which was added to the sample in known concentration. The concentrations of the native CDDs/CDFs were determined by comparing the above data with calibration curves prepared by plotting the analytical results obtained for a series of standards each of which contained a fixed concentration of internal standard but varying concentrations of representative CDDs and/or CDFs. More specifically, the ratio of the ion intensity recorded for the native CDD/CDF to the ion intensity obtained for the ^{37}Cl-labelled internal standard was plotted on the Y-axis vs. the ion intensity obtained for the ^{37}Cl-labelled internal standard. Since the ^{37}Cl-labelled internal standard was added at the beginning of the sample preparation/analysis scheme and, as indicated in the procedures outlined above, the internal standard was quantified at the same time as the native analyte(s), it is clear that the quantitative result obtained for the internal standard reflects losses of CDDs/CDFs incurred during the course of sample handling and analysis. However, the internal standard may not correct for the effects of the sample matrix, i.e. ^{37}Cl-labelled internal standard may not penetrate the sample

matrix and become sorbed or chemisorbed in the same fashion as, for example, CDDs/CDFs native to particulates which resulted from combustion. However the use of stable isotopically labelled internal standards as described above represents the state-of-the-art. In addition, as stated previously, the use of a stable-isotopically-labelled isomer to represent the several isomers in the same class or other different classes is based upon the assumption that the chemical/physical properties of the labelled isomer are parallel to those properties of the other isomers being quantitated.

During the analyses, it was necessary to establish criteria governing the identifications of CDDs/CDFs. These criteria are as follows:

(i) The mass chromatographic peaks produced by the component must exhibit appropriate GC retention times; that is, they must fall within a retention time "window" which has been established for a particular class of CDDs or CDFs (e.g., the tetrachlorinated dibenzo-p-dioxins, TCDDs). These "windows" were established by injecting available standards for each class of CDD and CDF, and also, in some instances, complex mixtures of standards containing CDD and/or CDF isomers which are known to be of a specific chlorinated class, but for which the actual isomeric structures have not been established. These time windows are shown in terms of elapsed time in Table 3.

(ii) Mass chromatograph peaks produced by the component must exhibit the appropriate response for at least two major m/z's which are characteristic (that is, are known to appear in the mass spectrum) of the particular CDD or CDF class being monitored (see Table 3). The ratio of relative intensities of the two ions monitored as indicators must correspond to that resulting from injection of an appropriate calibration standard within ±30%.

(iii) In cases where the sample matrix causes shifts in the GC retention times of the components of interest, as compared to the retention times of the corresponding standards determined from a separate injection of standards, and as indicated by analogous shifts in the retention times for the internal standards added to the sample, the identification of a specific CDD and/or CDF must be confirmed by coinjection of the sample with an added quantity of the CDD or CDF isomer in question. Enhancement of a given mass chromatographic peak upon such coinjection leads to tentative assignment of the unknown peak as a specific CDD or CDF isomer.

2. PCBs

The general approach for quantitation of PCBs present in the extracts of the samples was the same as that outlined for the CDDs/CDFs. However, in this case the internal standard employed was D_6-3,3',4,4'-tetrachlorobiphenyl and here again it was assumed, that the extraction, chromatographic and mass spectrometric behavior of all of the PCB's parallels that of the D_6-3,3',4,4'-TCB employed as an internal standard. The representative PCB standards listed later in this section were employed in calibrating the GC-MS in order to determine the gas chromatographic retention time "windows" appropriate for each class of PCBs as well as to determine mass spectral characteristics of each class. As in the case of the CDDs/CDFs, the assumption was made that the PCBs employed in the calibration of the GC-MS were indeed representative of all of the compounds comprising each of the ten classes of PCBs. This assumption can only be verified by exhaustive calibration employing all of the available PCB isomers; however, certified standards of all 209 isomers are not as yet available. The time windows which were used are shown in terms of elapsed time in Table 4.

The GC-MS-DS operational parameters employed for the quantification of PCBs are itemized below.

a. Conditions for he Gas Chromatograph

Column: 40M WCOT (OV-101) Fused Silica Capillary
Carrier Gas: Hydrogen, 30 lb. head pressure
Column Temperature: Programmed, 180° starting temperature and after 7 minutes program to 235° @ 5°C/min and hold at 235° for 50 minutes.
Interface Temperature: 250°C
Injector: Split @ 50:1

b. Conditions for the Mass Spectrometer

Ionizing Voltage: 70 eV
Accelerating Voltage: 4KV
Source Temperature: 250°C
Multiple Ion Monitoring Mode: See Table 4 for Details

c. Data Acquisition/Handling

Identical to that described for CDDs/CDFs.

TABLE 4. SEQUENCE OF OPERATIONS IN GC-MS-25 ANALYSES OF SAMPLE EXTRACTS FOR POLYCHLORINATED BIPHENYLS

Elapsed Time (min)	Event	GC Column Temp.	Temp. Program Rate (°C/min)	Ions Monitored By Mass Spectrometer (m/z)	Compounds Monitored
0.00	Injection, splitless	180°C	--		
1.50	Split valve on	190°C	--		
7.00	Open Column Flow to Mass Spec	190°C	--		
	Begin Temp. program to 270°	190°C	--		
	Start MID PROGRAM	190°C	5°C/min		
	Sweep Width = 100			188.039	Cl_1 PCBs
	Time on ion-mass = 0.1 sec			190.036	Cl_1 PCBs
	Time on D_6 -Tetrachlorobiphenyl ion-masses = 0.1 sec			222.000	Cl_2 PCBs
				223.997	Cl_2 PCBs
				255.961	Cl_3
				257.958	Cl_3
				289.922	Cl_4
				291.919	Cl_4
				325.880	Cl_5
				327.877	Cl_5
				359.841	Cl_6
				361.839	Cl_6
				393.802	Cl_7
				395.800	Cl_7
				427.763	Cl_8
				429.761	Cl_8
				463.722	Cl_9
				465.719	Cl_9
				497.683	Cl_{10}

(Continued)

TABLE 4 (Continued)

Elapsed Time (min)	Event	GC Column Temp.	Temp. Program Rate (°C/min)	Ions Monitored By Mass Spectrometer (m/z)	Compounds Monitored
				499.680	Cl_{10}
				295.922	D_6-Cl_4 labelled PCB
				297.919	D_6-Cl_4 labelled PCB
23.00	Hold Column Temp	270°C	--		
35.00	Stop MID PROGRAM	270°C	--		
40.00	Cool Column to Initial Temp.				

3. Chlorobenzenes

The general approach for quantitation of chlorobenzenes present in the extracts of the samples was the same as that approach outlined above for CDDs/CDFs. In this case $^{13}C_6$-hexachlorobenzene was employed as the internal standard and it was assumed that the behavior of this compound during extraction, chromatographic separation and mass spectrometric analyses parallels that of the other chlorobenzene isomers. As noted previously the chlorinated benzenes listed later in this section were assumed to be representative of the various classes of chlorobenzenes and these standards were employed to determine the retention window and ion-masses appropriate for quantitating the various classes of halobenzenes. The GC-MS-DS operational parameters appropriate for quantitation of the chlorobenzenes are outlined below. Time windows are listed in Table 5 in terms of retention time.

a. Conditions for the Gas Chromatograph

Column: 40M WCOT (OV-101) Fused Silica Capillary
Carrier Gas: Hydrogen, 30 lb. head pressure
Column Temperature: Programmed, 50°C starting temperature, hold for 2 minutes, program to 250° @ 8°/min.
Injector: Split @ 50:1
Interface Temperature: 250°C

b. Conditions for the Mass Spectrometer

Ionizing Voltage: 70 eV
Accelerating Voltage: 4KV
Source Temperature: 250°C
Multiple Ion Monitoring Mode: See Table 5 for Details

c. Data Acquisition/Handling

Identical to that described for CDDs/CDFs

4. Chlorophenols

The general approach for quantitation of the chlorinated phenols present in the extracts of the samples was the same as described previously for the CDD/CDFs. In this case $^{13}C_6$-pentachlorophenol was employed as the internal standard and in this case also it was assumed that the extraction, chromatographic, and mass spectrometric behavior of all of the chlorophenols parallels that of the $^{13}C_6$-pentachlorophenol employed as the internal standard. The chlorophenols listed later in this section were employed as calibration standards and were assumed to be representative of the various isomers comprising each of the classes of chlorophenols. Gas chromatographic retention time data and mass spectrometric

TABLE 5. SEQUENCE OF OPERATIONS IN GC-MS-25-DS ANALYSES OF SAMPLE EXTRACTS FOR CHLORINATED BENZENES

Elapsed Time (min)	Event	GC Column Temp.	Temp. Program Rate (°C/min)	Ions Monitored By Mass Spectrometer (m/z)	Compounds Monitored
0.00	Injection, splitless	60°C	--		
1.50	Split Valve on	60°C	--		
2.00	Begin Temperature Program to 250°	60°C	8°C/min		
7.00	Start MID PROGRAM Sweep = 500 Time on ion-mass = 0.1 sec Time on $^{13}C_6$-Hexachlorobenzene ion-masses = 0.1 sec	100°C	8°C/min	145.969 147.966 179.930 181.927 213.891 215.888 247.852 249.849 283.810 285.807 289.831 291.828	Cl_2 benzenes Cl_2 benzenes Cl_3 benzenes Cl_3 benzenes Cl_4 benzenes Cl_4 benzenes Cl_5 benzene Cl_5 benzene Cl_6 benzene Cl_6 benzene $^{13}C_6$-Cl_6 benzene $^{13}C_6$-Cl_6 benzene
22.00	Stop PROGRAM	220°C	--		
26.00	Final Temp.	250°C	--		
28.00	Cool Column to Initial Temp.				

data were obtained using the representative chlorophenols and the sequence of operations outlined in Table 6 was devised based upon these data. The GC-MS-DS operational parameters appropriate for the quantitation of the chlorophenols are listed below. Data on the retention time windows are presented in Table 6.

a. Conditions for the Gas Chromatograph

Column: 50M WCOT (OV-101) Fused Silica Capillary
Carrier Gas: Hydrogen, 30 lb. head pressure
Column Temperature: Programmed, 60°C starting temperature, Hold for 2 min., program to 250° @ 12°/min.
Injector: Split @ 50:1
Interface Temperature: 250°C

b. Conditions for the Mass Spectrometer

Ionizing Voltage: 70 eV
Accelerating Voltage: 4KV
Source Temperature: 250°C
Multiple Ion Monitoring Mode: See Table 6 for Details

c. Data Acquisition/Handling

Identical to that described for CDDs/CDFs.

The various chlorocarbon standards which were employed in this program included 9 CDD isomers, 7 CDF isomers, 13 PCB isomers, 6 chlorobenzene isomers, and 5 chlorophenol isomers. These standards and the sources from which they were obtained are presented in Table 7.

Aldehydes--

Aldehydes were analyzed in the impinger contents only. It is not known at this time whether water is an acceptable trapping medium for aldehydes. Since sodium bisulfite solution is recommended, it could be concluded that considerable oxidation of aldehydes would occur in a simple aqueous mixture. As a result, this procedure may yield data which actually represents the lower limits of true aldehyde concentrations.

The analytical procedure which was employed involved the extraction of the aldehydes, partitioning into acetonitrile, formation of dinitrophenylhydrazone derivatives, and detection and quantitation by High Performance Liquid Chromatography. The HPLC used for the analysis was the Varian Model 5021 HPLC described in "Halocarbons". The operational parameters during the analysis were as follows:

TABLE 6. SEQUENCE OF OPERATIONS IN GC-MS-25-DS ANALYSES OF SAMPLE EXTRACTS FOR CHLORINATED PHENOLS

Elapsed Time (min)	Event	GC Column Temp.	Temp. Program Rate (°C/min)	Ions Monitored By Mass Spectrometer (m/z)	Compounds Monitored
0.00	Injection, splitless	60°C	--		
1.50	Split valve on	60°C	--		
2.00	Begin Temperature Program to 250°	60°C	12°C/min		
10.00	Start MID PROGRAM	156°C	12°C/min	195.887	Cl_3 Phenols
10.00	Sweep = 500			197.884	Cl_3 Phenols
	Time on ion mass = 0.1 sec			229.867	Cl_4 Phenols
	Time on $^{13}C_6$ - Penta			231.864	Cl_4 Phenols
	Chlorophenol ion-mass = 0.1 sec			263.847	Cl_5 Phenol
				265.844	Cl_5 Phenol
		252°C		273.861	^{13}C-Cl_5 Phenol
18.00	Column Temp on Hold				
20.00	Stop PROGRAM				
25.00	Cool Column to Initial Temp.				

TABLE 7. HALOCARBON STANDARDS

CDD Isomers	
1,2,3,4-tetrachlorodibenzo-p-dioxin; Analabs, Inc., North Haven, CT	
$^{37}Cl_4$-2,3,7,8-TCDD; KOR Isotopes, Cambridge, MA	
2,3,7,8-TCDD and the 21 other TCDD isomers; Dow Chemical Co., Midland MI, and H. R. Buser, Swiss Federal Research Station, Wadenswil, Switzerland	
1,2,3,7,8-PCDD; KOR Isotopes, Cambridge, MA	
1,2,3,4,7,8-HxCDD; Dr. A. Poland, Univ. Rochester, NY	
1,2,3,4,6,7-HxCDD; KOR Isotopes, Cambridge, MA	
1,2,3,4,6,7,8-HpCDD; KOR Isotopes, Cambridge, MA	
OCDD; Analabs, Inc., North Have, MA	
$^{37}Cl_8$-OCDD; KOR Isotopes, Cambridge, MA	
CDF Isomers	
1,2,4,8-tetrachlorodibenzofuran	
2,3,7,8-tetrachlorodibenzofuran	All CDFs obtained from U.S. FDA Washington, DC
2,3,6,8-tetrachlorodibenzofuran	
1,2,4,7,8-pentachlorodibenzofuran	
1,2,4,6,7,9-hexachlorodibenzofuran	
1,2,3,4,6,8,9-heptachlorodibenzofuran	
Octachlorodibenzofuran	

(Continued)

TABLE 7 (Continued)

PCB Isomers	
4-Chlorobiphenyl	
3,3'-dichlorobiphenyl	
2,4',5-trichlorobiphenyl	
3,3',4,4'-tetrachlorobiphenyl	
2,2',6,6'-tetrachlorobiphenyl	
2,3,4,5,6-pentachlorobiphenyl	
2,2,',4,5,5'-pentachlorobiphenyl	Obtained from Ultra Scientific, Hope, RI
2,2',4,4',5,5'-hexachlorobiphenyl	
2,2',3,4,4',5',6-heptachlorobiphenyl	
2,2',3,3',4,4',5,5'-octachlorobiphenyl	
2,2',3,3',4,4',5,6,6'-nonachlorobiphenyl	
2,2',3,3',4,4',5,5',6,6'-decachlorobiphenyl	
D_6-3,3',4,4'-tetrachlorobiphenyl; KOR Isotopes, Cambridge, MA	

Chlorinated Benzenes	
$^{13}C_6$-hexachlorobenzene; KOR Isotopes, Cambridge, MA	
1,4-dichlorobenzene	
1,3,4-trichlorobenzene	
1,2,3,5-tetrachlorobenzene	Obtained from Ultra Scientific, Hope, RI
pentachlorobenzene	
hexachlorobenzene	

Chlorinated Phenols	
$^{13}C_6$-pentachlorophenol; KOR Isotopes, Cambridge, MA	
2,3,4-trichlorophenol	
2,3,4,5-tetrachlorophenol	Obtained from Ultra Scientific, Hope, RI
2,3,5,6-tetrachlorophenol	
pentachlorophenol	

Pressure: Minimum: 5 atm
Maximum: 250 atm

Injection Loop: 50 µL

Column: Guard: 37 Vydac SC Reverse Phase
Analytical: DuPont Zorbax-ODS
Temperature: Ambient

Director: Variachrom UV-Vis: 254 nm

Program:	Time	Code	Value
	0.0	%	80% Acetonitrile/20% Water
	0.0	Flow	1.4 mL/min.
	0.0	Event	Hold
	0.1	Event	Inject
	15.0	Event	Reset

As with the halocarbon analyses, standards were used to accurately identify and quantify the aldehydes. These standards, which were obtained from J. T. Baker Chemical Company, Obetz, Ohio and Supelco, Inc., Bellefonte, Pennsylvania are listed below.

Formaldehyde	Caproicaldehyde
Propionaldehyde	Benzaldehyde
Butyraldehyde	

SECTION 5

TEST PROGRAM RESULTS

HCL SAMPLING AND ANALYSIS

The results of the HCl emissions sampling and analysis are presented in Tables 8 and 9 for Sites A and B, respectively. The average hourly HCl emission rate from the mass fired incinerator was determined to be 6.1 kg/hr. The average using the primary sampling method for the RDF fired boiler was 7.6 kg/hr and it was 17.8 kg/hr using the modified Method 5 train. On a fuel consumption basis, emissions from the mass fired incinerator averaged 1.3 g HCl per kg of fuel and, from the RDF fired boiler emission rates averaged 0.9 g/kg when averaging the results of both sampling methods. For both units these emission rates were based on the average fuel feed rates of 4635 kg/hr and 8505 kg/hr for Sites A and B, respectively. Average firing rates were used because actual fuel feed data was not recorded during the test project.

With respect to variability over time, Site A exhibited the greatest overall variability with a relative standard deviation of 71%. Data from Site B, using the primary sampling method, yielded a relative standard deviation of 128% however this was heavily influenced by the questionably high value obtained from Test 3. Discounting this value, an average of 3.6 kg/hr with a relative standard deviation of 17% is obtained. Sampling with the modified Method 5 train was more erratic exhibiting a relative standard deviation of 62%. It is unclear however, whether the variability with time is due to changes in the actual HCl concentrations or due to problems with the sampling method. If it is assumed that the Method 5 variability is systematic in nature, the test data would indicate that HCl emissions are more stable from RDF fired boiler than from the mass fired incenerator. This would be reasonable because refuse derived fuel, because of the processing it undergoes, is more homogeneous with respect to such variables as the percent of chlorine containing compounds in the waste that is mass loaded raw waste.

The comparison of the two test methods used at Site B was inconclusive due to the limited size of the data base. Results using Method 5 train were higher in all tests than the concurrently operated primary method with results ranging from 3% to 375 percent higher with an average of 126%. The exact reason for this is unclear at this time but may be due to the collection of chloride containing particles on the filter and in the probe wash. In addition, the liquid volume in the impingers is 2.5 times

TABLE 8. HCL EMISSIONS DATA - SITE A

Test No.	Test Date	Sampling Duration (min)	Sample Volume (DSCM)	Total Cl^- (mg)	Stack Flow Rate (m^3/min)	HCl Concentration (ppm)	Emission Rate (kg/hr)	Emission Rate** (g/kg)
1	9/14/81	20	0.0344	4.54	453	90	3.7	0.8
2	9/14/81	20	0.0350	14.73	453	289	11.9	2.6
3	9/14/81	30	0.0511	13.30	490	176	7.9	1.7
4	9/14/81	30	0.0584	28.90	490	336	15.0	3.3
5	9/15/81	30	0.0566	5.94	399	71	2.6	0.6
6	9/15/81	30	0.0591	2.01	399	23	0.8	0.2
7	9/15/81	30	0.0495	2.93	399	40	1.5	0.3
8	9/15/81	30	0.0491	6.88	499	95	4.3	0.9
9	9/15/81	30	0.0493	10.97	490	151	6.7	1.5
10*	9/21/81	30	0.0453	1.49	649	22	1.3	0.3
11*	9/21/81	36	0.0615	5.69	643	63	3.7	0.8
12	9/21/81	42	0.0554	7.27	538	89	4.4	1.0
13	9/21/81	35	0.0675	10.02	538	112	5.5	1.2
14	9/22/81	30	0.0605	16.31	555	183	9.2	2.0
15	9/22/81	30	0.0604	8.40	550	94	4.7	1.0
16	9/22/81	30	0.0491	7.72	552	107	5.4	1.2
17	9/22/81	32	0.0587	24.91	552	228	14.5	3.2

*Unit experiencing operational difficulties resulting from inefficient combustion of excessively wet refuse. ** g of HCl/Kg of refuse burned.

TABLE 9. HCL EMISSIONS DATA - SITE B

Test No	Test Date	Sampling Duration (min)	Sample Volume (DSCM)	Total Cl^- (mg)	Stack Flow Rate (m^3/min)	HCl Concentration (ppm)	Emission Rate (kg/hr)	Emission Rate** (g/kg)
1A	6/17/82	30	0.0564	2.42	1366	29	3.6	0.4
1B	6/17/82	30	0.4245	19.00	1366	30	3.7	0.4
2A	6/17/82	30	0.0578	2.21	1366	26	3.2	0.4
2B	6/17/82	30	0.4315	77.70	1366	122	15.2	1.8
3A	6/17/82	30	0.0555	17.37	1403	212	27.0	3.2
3B	6/17/82	--**	--	--	--	--	--	--
4A	6/18/82	30	0.0530	3.20	1218	41	4.5	0.5
5B	6/18/82	30	0.4339	28.45	1218	44	4.9	0.6
5A	6/18/82	30	0.0495	2.00	1218	27	3.0	0.4
5B	6/18/82	30	0.4108	27.79	1218	46	5.1	0.6
6A	6/18/82	30	0.0506	2.33	1302	31	3.7	0.4
6B	6/18/82	30	0.4108	51.70	1302	85	10.1	1.2

*A = primary sampling method.
B = modified Method 5 train.

**Equipment malfunction

***g of HCl/Kg of refuse burned

that of the midget impingers used in the primary method. As a result, since only 20 ml of sample is actually titrated, any error in titration is amplified to a much larger extent. This problem can be easily avoided by titrating larger aliquots. The particulate chloride interference problem bears further investigation.

ORGANIC COMPOUND SAMPLING AND ANALYSIS

As stated previously, all organic compound emissions testing was conducted using a modified EPA Method 5 sampling system. Three tests were conducted at Site A and four tests at Site B. The last two tests at Site B were shorter than desired due to plant process problems. As a result the samples from these two tests were combined in order to ensure a sufficient quantity of compounds for analysis. All data from these tests are combined and presented as Test 3.

A sampling data summary for all of the Method 5 type tests is presented in Table 10. As shown on this table, all tests were well within the limits of 90 to 110% isokinetic variations.

The remainder of this section presents the emissions data for the organic compounds which were sampled and analyzed. Because of the diversity of the data, each class of compounds is discussed separately. When presenting results averages, only the samples that includes analysis of all of the fractions were used.

Chlorinated Dibenzo-p-Dioxins (CDDs)

The results of the emissions sampling for CDDs are presented in Table 11. Emissions of total CDDs averaged approximately 152 mg/hr and 33 µg/kg of fuel from the mass fired water wall incinerator (Site A) and approximately 3.7 mg/hr and 0.4 µg/kg of fuel from the RDF fired stoker boiler (Site B). On an annual basis these emission rates equate to approximately 1.3 kg/year from Site A and 0.03 kg/year from Site B.

The isomeric distribution of the CDDs was similar for the two types of systems with the majority of the emissions in the form of heptachlorinated dibenzo-p-dioxins. For the RDF fired boiler at least 50% of the CDD emissions were HpCDD with the next highest being octachlorinated compounds. Together, HpCDD and OCDD emissions accounted for 80% or more of the total CDD emissions.

This trend toward the heavier compounds was also presented in the mass fired incinerator samples but to a lesser extent. HpCDD was again the major class of CDDs present however, hexachlorinated dioxins were the next major component followed by pentachlorinated, and tetrachlorinated dioxins with OCDD being present in the smallest quantities.

Within each of the 5 classes of dioxins analyzed the number of apparent isomers which were detected at Site A ranged from 1 to 11 as shown in Table 12. A more detailed evaluation of the isomeric distribution of tetrachlorinated dibenzo-p-dioxins is presented in Table 13. As shown, the major isomers present are the 1, 3, 6, 8 and 1, 3, 7, 9 isomers.

TABLE 10. METHOD 5 SAMPLING DATA SUMMARY

	Site A	Site A	Site A
Run No.	Test 1	Test 2	Test 3
Date	9/15/81	9/21/81	9/22/81
Volume of Gas Sampled (DSCM)	2.938	4.517	6.814
Test Time (min)	180	180	300
Stack Area (m^2)	1.17	1.17	1.17
Stack Gas Velocity (m/min)	762.9	1165.3	1044.2
Stack Gas Temperature (°C)	269	267	288
Stack Gas Moisture (%)	17.4	12.1	14.0
Stack Gas Mol. Wt. (g/mole)	27.66	27.77	28.29
Stack Gas Flow Rate (m^3/min)	400	650	550
Nozzle Diameter (cm)	0.767	0.767	0.767
Isokinetic Variation (%)	103	97	104
Gas Analysis			
Carbon Dioxide (%)	7.8	2.5	9.4
Oxygen (%)	11.0	18.0	11.4
Nitrogen (%)	81.2	79.5	79.2
Particulates - Total			
mg	375	2047	2045
mg/m^3	128	453	300
kg/hr	3.1	17.8	9.9

Standard Conditions: 20°C, 760 mm Hg

TABLE 10 (Continued)

	Site B	Site B	Site B
Run No.	Test 1	Test 2	Test 3
Date	6/17/82	6/17/82	6/18/82
Volume of Gas Sampled (DSCM)	4.619	4.536	5.062
Test Time (min)	200	200	260
Stack Area (m^2)	4.15	4.15	4.15
Stack Gas Velocity (m/min)	631.2	643.4	590.4
Stack Gas Temperature (°C)	233	233	241
Stack Gas Moisture (%)	7.63	6.59	7.45
Stack Gas Mol. Wt. (g/mole)	28.87	28.68	28.98
Stack Gas Flow Rate (m^3/min)	1365	1400	1260
Nozzle Diameter (cm)	0.767	0.767	0.767
Isokinetic Variation (%)	101	96	100
Gas Analysis			
Carbon Dioxide (%)	8.0	5.5	9.4
Oxygen (%)	12.0	14.0	9.0
Nitrogen (%)	80.0	80.5	81.6
Particulates - Total			
mg	102.0	22.6	15.6
mg/m^3	22.1	5.0	3.1
kg/hr	1.81	0.42	0.23

Standard Conditions: 20°C, 760 mm Hg

TABLE 11. CHLORINATED DIBENZO-P-DIOXINS EMISSIONS SUMMARY

Test/Compound	Test Date	Sample Volume (DSCM)	Compound Quantity (ng)	Stack Flow Rate (m^3/min)	Concentration (ng/m^3)	Emission Rate (mg/hr)	Emission Rate (µg/kg)
Site A, Test 1*	9/15/81	2.938	--	400	--	--	--
Tetra-CDDs	--	--	770	--	253	6.06	1.31
Penta-CDDs	--	--	650	--	222	5.32	1.15
Hexa-CDDs	--	--	730	--	248	5.94	1.28
Hepta-CDDs	--	--	1,060	--	362	8.67	1.87
Octa-CDDs	--	--	440	--	151	3.62	0.78
Total CDDs	--	--	3,650	--	1,236	29.61	6.39
Site A, Test 2	9/21/81	4,517	--	650	--	--	--
Tetra-CDDs	--	--	3,160	--	700	27.42	5.92
Penta-CDDs	--	--	4,150	--	919	36.00	7.77
Hexa-CDDs	--	--	6,970	--	1,544	60.48	13.05
Hepta-CDDs	--	--	3,450	--	765	29.97	6.47
Octa-CDDs	--	--	910	--	201	7.87	1.70
Total CDDs	--	--	18,640	--	4,129	161.74	34.91
Site A Test 3	9/22/81	6.814	--	550	--	--	--
Tetra-CDDs	--	--	2,560	--	376	12.44	2.68
Penta-CDDs	--	--	3,640	--	534	17.66	3.81
Hexa-CDDs	--	--	5,800	--	851	28.15	6.07
Hepta-CDDs	--	--	13,940	--	2,045	67.64	14.59
Octa-CDDs	--	--	3,340	--	491	16.24	3.50
Total CDDs	--	--	29,280	--	4,297	142.13	30.65

*Impinger contents not analyzed.

TABLE 11 (Continued)

Test/Compound	Test Date	Sample Volume (DSCM)	Compound Quantity (ng)	Stack Flow Rate (m^3/min)	Concentration (ng/m^3)	Emission Rate (mg/hr)	Emission Rate (µg/kg)
Site B, Test 1	6/17/82	4.619	--	1,365	--	--	--
Tetra-CDDs	--	--	3	--	0.6	0.05	0.006
Penta-CDDs	--	--	2	--	0.4	0.03	0.004
Hexa-CDDs	--	--	6	--	1.3	0.11	0.013
Hepta-CDDs	--	--	94	--	20.4	1.67	0.196
Octa-CDDs	--	--	57	--	12.3	1.01	0.119
Total CDDs	--	--	162	--	35.0	2.87	0.338
Site B, Test 2**	6/17/82	4.536	--	1,400	--	--	--
Tetra-CDDs	--	--	2	--	0.4	0.03	0.004
Penta-CDDs	--	--	2	--	0.4	0.03	0.004
Hexa-CDDs	--	--	3	--	0.7	0.06	0.007
Hepta-CDDs	--	--	15	--	3.3	0.28	0.033
Octa-CDDs	--	--	13	--	2.9	0.24	0.028
Total CDDs	--	--	35	--	7.7	0.64	0.076
Site B, Test 3***	6/18/82	5.062	--	1,260	--	--	--
Tetra-CDDs	--	--	19	--	3.9	0.29	0.034
Penta-CDDs	--	--	15	--	3.0	0.23	0.027
Hexa-CDDs	--	--	28	--	5.5	0.42	0.049
Hepta-CDDs	--	--	162	--	32.0	2.42	0.285
Octa-CDDs	--	--	81	--	16.0	1.21	0.142
Total CDDs	--	--	305	--	60.3	4.57	0.537

**Methanol front and back and toluene back washes not analyzed.

***Data represents a composite of Tests 3 and 4.

TABLE 12. NUMBER OF APPARENT ISOMERS IN EACH CLASS OF CDDs FOUND IN THE EXTRACT OF PARTICULATE FILTER, TOLUENE WASH/FRONT OF SAMPLING TRAIN[a]

CDDs Class	No. of Isomers Detected[b]
TCDDs	11
PCDDs	8
HxCDDs	8
HpCDDs	1
OCDD	1

[a]Isomers were identified on the basis of gas chromatographic retention times and relative abundances of the two principal ion-masses in the molecular ion cluster. Where possible, gas chromatographic and mass spectrometric data obtained for an extract were compared with similar data obtained for authentic standards available in the Brehm Laboratory, and identifications were made on the basis of these direct comparisons. Where specific isomer standards were not available, the identity of a peak in the mass chromatogram was inferred by comparisions with data for other closely-related isomers. Until a laboratory possesses all isomers for a given class of CDDs and demonstrates the ability to separate these, no unequivocal identification of specific isomers can be made.

[b]These numbers represent the minimum numbers of isomers detected because, in some cases, several isomers elute simultaneously thus a given peak may represent one or several isomers.

TABLE 13. SPECIFIC TCDD ISOMERS IDENTIFIED IN THE EXTRACT OF PARTICULATE FILTER, TOLUENE WASH/FRONT OF SAMPLING TRAIN FROM SITE A

TCDD Isomer	% of Total TCDDs
1,3,6,8	20.97
1,3,7,9	13.29
1,3,6,9	5.17
1,3,7,9/1,4,6,9/1,2,4,7/1,2,4,8[a]	10.64
1,2,4,6/1,2,4,9	14.77
1,2,6,8	7.09
1,4,7,8	6.65
1,2,7,9	2.07
1,2,3,4/1,2,3,6/1,2,6,9[b]	11.08
1,2,3,7/1,2,3,8/2,3,7,8[c]	3.84
1,2,7,8	4.43
	100%

[a]Using the OV-101 WCOT glass capillary column, the 1,3,7,8-TCDD; 1,4,6,9-TCDD; 1,2,4,7-TCDD and 1,2,4,8-TCDD isomers are resolved from the other TCDD isomers but are not resolved from each other. Therefore, the quantity of TCDDs identified here could arise from one or more of these four unresolved isomers.

[b]Using the OV-101 WCOT glass capillary column, the 1,2,3,4-TCDD; 1,2,3,6-TCDD; and 1,2,6,9-TCDD isomers are resolved from the other TCDD isomers but are not resolved from each other. Therefore, the quantity of TCDDs identified here could arise from one or more of these three unresolved isomers.

[c]Using the OV-101 WCOT glass capillary column, the 1,2,3,7-TCDD; 1,2,3,8-TCDD; and 2,3,7,8-TCDD isomers are resolved from the other TCDD isomers but are not resolved from each other. Therefore, the quantity of TCDDs identified here could arise from one or more of these three unresolved isomers.

An evaluation of the migration of the CDDs through the sampling train revealed that the majority of the CDDs were found in the back half (down stream of the filter) of the Method 5 train, specifically in the impinger contents and the back half toluene wash. Only a very small amount made it all the way through to the XAD-2 resin trap. Very little was found in any of the methanol washes of either the front or back halves of the train. The quantity of CDDs found on the particulate filters and in the front half toluene washes varied from non-detectable quantities to 100% of the total of each class of CDDs. Two tests, one on each source, yielded data showing the majority of CDDs to be present in the front half of the train. In both cases these were tests with relatively high particulate catches. Another sampling phenomenon which the data revealed was the tendency for lighter CDDs to move farther through the sample train than the heavier CDDs. In most cases the vast majority of the OCDDs were found on the filter and in the front half wash whereas most TCDDs were found in the impinger contents and back half toluene washes. TCDDs were also found in the greatest quantities on the XAD-2 resin trap. No appreciable difference in the sampling train collection characteristics was noted between the mass fired and RDF fired units. Data showing the distribution of CDDs in the sample train are presented in Appendix B.

As a summary of the CDD data, emissions from the RDF fired boiler were considerably less than those from the mass fired water wall incinerator. Isomeric distributions were similar but emissions from the RDF fired boiler exhibited a stronger tendency toward hepta- and octa-CDDs than did the mass fired incinerator. Sample train collection efficiency appeared to be high in both cases with very small quantities of the CDDs passing through to the XAD-2 resin trap. Most compounds were detected in the back half of the sample train in the impingers and in the toluene back half wash.

Chlorinated Dibenzofurans (CDFs)

The results of the emissions sampling for CDFs are presented in Table 14. Emissions of total CDFs averaged approximately 263 mg/hr and 57 µg/kg of fuel from the mass fired water wall incinerator and approximately 8.5 mg/hr and 1.0 µg/kg of fuel from the RDF fired boiler. On an annual basis these emission rates equate to approximately 2.3 kg/year from Site A and 0.07 kg/year from Site B.

The isomeric distribution of the CDFs differed for the two types of units. The majority of the CDF emissions from Site A were tetrachlorinated followed by hexachlorinated and pentachlorinated. CDF emissions from Site B were primarily heptachlorinated followed by tetrachlorinated. TCDFs comprised approximately 41% of all CDF emissions from Site A and HpCDFs comprised approximately 50% of the total CDF emissions from Site B.

This isomeric distribution is in contrast to that reported for CDDs where both units exhibited tendencies toward heavier compounds. For CDF emissions the mass fired unit (Site A) exhibited strong tendencies

TABLE 14. CHLORINATED DIBENZOFURANS EMISSIONS SUMMARY

Test/Compound	Test Date	Sample Volume (DSCM)	Compound Quantity (ng)	Stack Flow Rate (m^3/min)	Concentration (ng/m^3)	Emission Rate (mg/hr)	Emission Rate (µg/kg)
Site A, Test 1*	9/15/81	2.938	--	400	--	--	--
Tetra-CDFs	--	--	2,050	--	697	16.69	3.60
Penta-CDFs	--	--	790	--	270	6.47	1.40
Hexa-CDFs	--	--	1,260	--	429	10.27	2.22
Hepta-CDFs	--	--	1,650	--	562	13.46	2.90
Octa-CDFs	--	--	100	--	33	0.79	0.17
Total CDFs	--	--	5,850	--	1,991	47.68	10.29
Site A, Test 2	9/21/81	4.517	--	650	--	--	--
Tetra-CDFs	--	--	14,650	--	3,244	127.08	27.42
Penta-CDFs	--	--	5,220	--	1,155	45.25	9.76
Hexa-CDFs	--	--	6,320	--	1,399	54.80	11.82
Hepta-CDFs	--	--	2,660	--	588	23.03	4.97
Octa-CDFs	--	--	140	--	32	1.25	0.27
Total CDFs	--	--	28,990	--	6,418	250.69	54.24
Site A, Test 3	9/22/81	6.814	--	550	--	--	--
Tetra-CDFs	--	--	17,670	--	3,594	85.80	18.51
Penta-CDFs	--	--	11,000	--	1,615	53.42	11.53
Hexa-CDFs	--	--	12,050	--	1,768	58.48	12.62
Hepta-CDFs	--	--	15,000	--	2,203	72.87	15.72
Octa-CDFs	--	--	1,160	--	170	5.62	1.21
Total CDFs	--	--	56,880	--	8,350	276.19	59.59

*Impinger contents not analyzed.

TABLE 14 (Continued)

Test/Compound	Test Date	Sample Volume (DSCM)	Compound Quantity (ng)	Stack Flow Rate (m^3/min)	Concentration (ng/m^3)	Emission Rate (mg/hr)	Emission Rate (µg/kg)
Site B, Test 1	6/17/82	4.619	--	1,365	--	--	--
Tetra-CDFs	--	--	50	--	10.6	0.87	0.102
Penta-CDFs	--	--	15	--	3.0	0.25	0.029
Hexa-CDFs	--	--	30	--	6.5	0.53	0.062
Hepta-CDFs	--	--	180	--	23.4	1.92	0.226
Octa-CDFs	--	--	30	--	7.1	0.58	0.068
Total CDFs	--	--	305	--	50.6	4.15	0.487
Site B, Test 2**	6/17/82	4.536	--	1,400	--	--	--
Tetra-CDFs	--	--	40	--	8.2	0.69	0.081
Penta-CDFs	--	--	15	--	3.3	0.28	0.033
Hexa-CDFs	--	--	20	--	4.4	0.37	0.044
Hepta-CDFs	--	--	40	--	8.6	0.72	0.085
Octa-CDFs	--	--	7	--	1.5	0.13	0.015
Total CDFs	--	--	122	--	26.0	2.19	0.258
Site B, Test 3	6/18/82	5.062	--	1,260	--	--	--
Tetra-CDFs	--	--	160	--	30.8	2.33	0.274
Penta-CDFs	--	--	75	--	14.6	1.10	0.129
Hexa-CDFs	--	--	120	--	23.3	1.76	0.207
Hepta-CDFs	--	--	470	--	93.0	7.03	0.827
Octa-CDFs	--	--	40	--	7.5	0.57	0.067
Total CDFs	--	--	865	--	169.2	12.79	1.504

**Methanol front and back and toluene back washes not analyzed.

toward lighter compounds with 60% of all measured CDFs being less than hexachlorinated while the RDF fired unit (Site B) moved toward heavier compounds with 60% of the CDFs being more than hexachlorinated.

Within each of the 5 classes of CDFs analyzed the number of apparent isomers which were detected ranged from 1 to 17 as shown in Table 15. Though the relative abundance of each class of CDFs differed between the units, the number of isomers within each class remmained the same.

The migration of the CDFs through the sampling train was quite similar to that of the CDDs as shown in Appendix B. Most CDFs were found in the back half of the train in the impinger contents and back half toluene wash. As with the CDDs, only a small amount of CDFs made it all the way through to the XAD-2 resin trap and very little was found in any of the methanol washes of either the front or back halves of the train. The quantity of CDFs found on the particulate filter and in the front half toluene washes varied from 1% to 100% of the total for each class of CDFs.

As with the CDDs, lighter CDFs tended to move farther through the sampling train than the heavier CDFs. In most cases the majority of the OCDFs were found in the front half of the train whereas most TCDFs were found in the back half. TCDFs were also found in the greatest quantities on the XAD-2 resin trap.

No appreciable difference in the sampling train collection characteristics were noted between the mass fired and RDF fired units except that the tendency of heavier compounds to be collected in the front of the train was somewhat less pronounced at Site B than it was at Site A.

As a summary of the CDF data, emissions from the RDF fired boiler were considerable less than those from the mass fired water wall incinerator. Isomeric distributions differed for the two units in that the majority of emissions from Site A were tetrachlorinated and the majority from Site B were heptachlorinated. Aproximately 60% of the CDF emissions from Site A were less thaen hexachlorinated whereas 60% of the CDF emissions form Site B were greater than hexachlorinated. Sample train collection efficiency appeared to be high in both cases with very small quantities of the CDFs passing through to the XAD-2 resin trap. Most compounds were detected in the back half of the sample train in the impingers and in the toluene back half wash.

Chlorobenzenes

The results of the emissions sampling for chlorobenzenes are presented in Table 16. Emissions of total chlorobenzenes varied considerably from test to test and averaged approximately 1890 mg/hr and 408 µg/kg of fuel from Site A and approximately 9 mg/hr and 1.1 µg/kg of fuel from Site B. On an annual basis these emissions equate to approximately 16.6 kg/year from Site A and 0.08 kg/year from Site B. These averages are of data only from those tests in which all sample fractions were analyzed.

TABLE 15. NUMBER OF APPARENT ISOMERS IN EACH CLASS OF CDFs FOUND IN THE EXTRACT OF PARTICULATE FILTER, TOLUENE WASH/FRONT OF SAMPLING TRAIN[a]

CDFs Class	No. of Isomers Detected
TCDFs	17
PCDFs	12
HxCDFs	11
HpCDFs	4
OCDF	1

[a]Isomers were identified on the basis of gas chromatographic retention times and relative abundances of the two principal ion-masses in the molecular ion cluster. Where possible, gas chromatographic and mass spectrometric data obtained for an extract were compared with similar data obtained for authentic standards available in the Brehm Laboratory, and identifications were made on the basis of these direct comparisons. Where specific isomer standards were not available, the identity of a peak in the mass chromatogram were inferred by comparisons with data for other closely-related isomers. Until a laboratory possesses all isomers for a given class of CDFs and demonstrates the ability to separate these, no unequivocal identification of specific isomers can be made.

TABLE 16. CHLOROBENZENES EMISSIONS SUMMARY

Test/Compound	Test Date	Sample Volume (DSCM)	Compound Quantity (ng)	Stack Flow Rate (m^3/min)	Concentration (ng/m^3)	Emission Rate (mg/hr)	Emission Rate (µg/kg)
Site A, Test 1*	9/15/81	2.938	--	400	--	--	--
Di-ClBs	--	--	13	--	4	0.10	0.02
Tri-ClBs	--	--	1,470	--	500	12.00	2.59
Tetra-ClBs	--	--	8,100	--	2,760	66.00	14.24
Penta-ClBs	--	--	19,360	--	6,590	157.78	34.04
Hexa-ClBs	--	--	5,850	--	1,990	47.72	10.30
Total ClBs	--	--	34,793	--	11,844	283.60	61.19
Site A, Test 2	9/21/81	4.517	--	650	--	--	--
Di-ClBs	--	--	2,670	--	590	23.15	4.99
Tri-ClBs	--	--	4,820	--	1,070	41.80	9.02
Tetra-ClBs	--	--	6,130	--	1,360	53.20	11.48
Penta-ClBs	--	--	22,500	--	4,980	194.89	42.05
Hexa-ClBs	--	--	8,320	--	1,840	72.20	15.58
Total ClBs	--	--	44,440		9,840	385.24	83.12
Site A, Test 3	9/22/81	6.814	--	550	--	--	--
Di-ClBs	--	--	30,000	--	4,400	145.64	31.42
Tri-ClBs	--	--	130,000	--	19,000	629.11	135.73
Tetra-ClBs	--	--	195,000	--	28,600	946.06	204.11
Penta-ClBs	--	--	268,000	--	39,300	1,300.99	280.69
Hexa-ClBs	--	--	77,000	--	11,300	373.98	80.69
Total ClBs	--	--	700,000	--	102,600	3,395.78	732.64

*Impinger contents not analyzed.

TABLE 16 (Continued)

Test/Compound	Test Date	Sample Volume (DSCM)	Compound Quantity (ng)	Stack Flow Rate (m^3/min)	Concentration (ng/m^3)	Emission Rate (mg/hr)	Emission Rate (µg/kg)
Site B, Test 1	6/17/82	4.619	--	1,365	--	--	--
Di-ClBs	--	--	36	--	8	0.64	0.075
Tri-ClBs	--	--	260	--	56	4.56	0.536
Tetra-ClBs	--	--	260	--	57	4.66	0.548
Penta-ClBs	--	--	ND	--	--	--	--
Hexa-ClBs	--	--	44	--	10	0.78	0.092
Total ClBs	--	--	600	--	131	10.64	1.251
Site B, Test 2**	6/17/82	4.536	--	1,400	--	--	--
Di-ClBs	--	--	1	--	0	0.02	0.002
Tri-ClBs	--	--	650	--	144	12.12	1.425
Tetra-ClBs	--	--	1,000	--	222	18.70	2.199
Penta-ClBs	--	--	6,330	--	1,395	117.43	13.807
Hexa-ClBs	--	--	3,230	--	712	59.94	7.048
Total ClBs	--	--	11,211	--	2,473	208.21	24.481
Site B, Test 3	6/18/82	5.062	--	1,260	--	--	--
Di-ClBs	--	--	10	--	2	0.15	0.018
Tri-ClBs	--	--	39	--	8	0.58	0.068
Tetra-ClBs	--	--	34	--	7	0.51	0.060
Penta-ClBs	--	--	142	--	28	2.12	0.249
Hexa-ClBs	--	--	278	--	55	4.15	0.488
Total ClBs	--	--	503	--	100	7.51	0.883

**Methanol front and back and toluene back washes not analyzed.

ND - None Detected. Detection limits = 1.0 ng for Methanol Wash and Filter, and 20 ng for Impinger Catch, Toluene Wash, and XAD-2 Trap.

The isomeric distribution of the chlorobenzenes was different for the two units tested. Pentachlorobenzene was the primary compound detected in all three tests of Site A with tetrachlorobenzene being the compound found in the second highest quantity in two of the tests and hexachlorobenzene in the third. Emissions from Site B exhibited no such correlation with all three tests yielding different highest and second highest compounds. Pentachlorobenzene was present in the highest quantity in one test and in the second highest in another, as was hexachlorobenzene. Based on the average of the three tests at Site B, 58% of the measured chlorobenzenes were penta- or hexachlorinated thus a tendency toward heavier compounds was present as it was at Site A. The dominance of one specific class of chlorobenzenes was not present at Site B, however, as it was at Site A.

The vast majority of the chlorobenzenes were found in the XAD-2 resin trap of the sampling train as shown in Appendix B. Those chlorobenzenes not captured in the trap were found primarily in the impinger contents and back half toluene wash. Very little was detected in the front half from any of the tests and what was found there was mostly tetrachlorobenzene or heavier chlorobenzenes. No difference in the sample train distribution was noted between the results from Sites A and B.

In summary, as with CDDs and CDFs, the chlorobenzene emissions from Site A were much higher than those from Site B with Site B emissions exceeding Site A emissions by a factor of approximately 99 on a µg/kg of fuel basis. The isomeric destribution also differed for the two sites with Site A emitting pentachlorobenzene in the greatest quantities in all tests whereas Site B appeared less stable with different compounds being emitted in the greatest quantities in the different tests. A trend toward the heavier chlorobenzenes was present at both sites. In all tests, most chlorobenzenes were collected in the XAD-2 resin trap with lesser amounts in the impingers.

Chlorophenols

The results of the emissions sampling for chlorophenols are presented in Table 17. Emissions of total chlorophenols averaged approximately 5891 mg/hr and 1271 µg/kg of fuel from Site A and approximately 935 mg/hr and 110 µg/kg of fuel from Site B. On an annual basis these emissions equate to approximately 51.6 kg/year from Site A and 8.2 kg/year from Site B. As with the chlorobenzenes there was a considerable amount of variation in the measured concentrations among the tests.

The isomeric distribution of the chlorophenols was different for the two units tested. Trichlorophenol was the primary compound detected in all three tests of Site A with tetrachlorophenol a distant second. Emissions from Site B varied from test to test with the first test yielding similar quantities of tri, tetra and pentachlorophenols; the second test showing tetrachlorophenol being slightly higher than the others and test 3 indicating significantly higher quantities of pentachlorophenol. Overall, the emissions from Site A exhibited a tendency toward the lighter chlorophenols and Site B exhibited a tendency toward the heavier chlorophenols.

TABLE 17. CHLOROPHENOLS EMISSIONS SUMMARY

Test/Compound	Test Date	Sample Volume (DSCM)	Compound Quantity (ng)	Stack Flow Rate (m^3/min)	Concentration (ng/m^3)	Emission Rate (mg/hr)	Emission Rate (µg/kg)
Site A, Test 1*	9/15/81	2.938	--	400	--	--	--
Tri-CPs	--	--	57,500	--	19,600	469	101.1
Tetra-CPs	--	--	17,100	--	5,800	140	30.1
Penta-CPs	--	--	10,600	--	3,600	87	18.7
Total CPs	--	--	85,200	--	29,000	696	149.9
Site A, Test 2	9/21/81	4.517	--	650	--	--	--
Tri-CPs	--	--	300,000	--	66,300	2,600	560.1
Tetra-CPs	--	--	128,000	--	28,400	1,100	240.2
Penta-CPs	--	--	38,800	--	8,600	340	72.6
Total CPs	--	--	466,800	--	103,300	4,040	872.9
Site A, Test 3	9/22/81	6,814	--	550	--	--	--
Tri-CPs	--	--	479,000	--	129,000	4,300	920.8
Tetra-CPs	--	--	438,000	--	64,300	2,100	459.1
Penta-CPs	--	--	276,000	--	40,600	1,300	289.5
Total CPs	--	--	1,193,000	--	233,900	7,700	1,669.4

*Impinger contents not analyzed.

TABLE 17 (Continued)

Test/Compound	Test Date	Sample Volume (DSCM)	Compound Quantity (ng)	Stack Flow Rate (m^3/min)	Concentration (ng/m^3)	Emission Rate (mg/hr)	Emission Rate (µg/kg)
Site B, Test 1	6/17/82	4.619	--	1,365	--	--	--
Tri-CPs	--	--	15,900	--	3,433	281.3	33.1
Tetra-CPs	--	--	13,900	--	3,005	246.2	28.9
Penta-CPs	--	--	13,500	--	2,913	238.7	28.1
Total CPs	--	--	43,300	--	9,351	766.2	90.1
Site B, Test 2**	6/17/82	4,536	--	1,400	--	--	--
Tri-CPs	--	--	4,100	--	906	76.3	9.0
Tetra-CPs	--	--	5,700	--	1,259	106.0	12.5
Penta-CPs	--	--	5,100	--	1,117	94.0	11.1
Total CPs	--	--	14,900	--	3,282	276.3	32.6
Site B, Test 3	6/18/82	5.062	--	1,260	--	--	--
Tri-CPs	--	--	5,900	--	1,174	88.7	10.4
Tetra-CPs	--	--	19,500	--	3,856	291.5	34.3
Penta-CPs	--	--	48,400	--	9,564	723.0	85.0
Total CPs	--	--	73,800	--	14,594	1,103.2	129.7

**Methanol front and back and toluene back washes not analyzed.

As with all other compounds discussed thus far, most chlorophenols were detected in the back half components of the sample train, primarily in the impinger contents and XAD-2 resin trap. Large quantities were also found in the toluene wash of the back half. Very little was found in the front half from any of the tests. No difference in the sample train distribution was noted between the results from Sites A and B. Data showing the distribution of CPs in the sample train are presented in Appendix B.

As a summary, the chlorophenol emissions from Site A were considerably higher than those from Site B. The magnitude of the difference, while substantial, is the least of any of the compounds discussed thus far. The isomeric distribution differed for the two sites with Site A emitting trichlorophenol in the greatest quantity in all tests and Site B emitting differing mixes of chlorophenols. In general, Site A emitted more in the way of lighter chlorophenols and Site B emitted more of the heavier chlorophenols. Sample train collection characteristics were the same for both sites. Most chlorophenols were collected in the impingers with lesser amounts in the XAD-2 resin trap.

Polychlorinated Biphenyls (PCBs)

PCB emissions were detected only at Site A and in only 2 of the 3 tests at that location. PCB concentrations in all other tests were below the analytical detection limit of 10 ng per sample for each class of compounds. The emissions data from these two tests are presented in Table 18. As shown, only tri, tetra, hexa and heptachlorinated biphenyls were detected although analysis was conducted for all 10 classes of PCBs. The emitted quantities differed considerably with one test yielding 42.5 mg/hr (9.1 µg/kg of fuel) and the other yielding 8.5 mg/hr (1.8 µg/kg of fuel). The isomeric distribution also differed with TrCB accounting for 65% and TeCB, 34% of the emissions from test 1 while the emissions from test 2 were 32%, 29%, 20% and 19% PeCB, TeCB, TrCB and HxCB, respectively. This along with the varying emission rates and the fact that PCBs were detected in only 2 of the 3 tests at Site A and not at all at Site B leads to the conclusion that the PCBs are not emitted on a regular or stable basis from such waste fired incinerators and boilers. Of these PCBs that were emitted, most were detected in the impinger contents, back half toluene wash and XAD-2 resin trap as shown in Appendix B.

Aldehydes

Total aldehydes emissions data are presented in Table 19. As shown, aldehydes are emitted in much larger quantities than any of the chlorinated organic compounds presented above. Aldehyde emissions from Site A averaged 166 g/hr and 36 mg/kg of fuel and from Site B averaged 9 g/hr and 1 mg/kg. On an annual basis these emissions equate to approximately 1454 kg/year from Site A and 79 kg/year from Site B. Emission rates varied considerably at both sites but especially at Site A. Analysis was only conducted on the impinger contents because it is expected that any aldehydes not trapped in the impingers would be oxidized to acids and would not be detectable.

TABLE 18. POLYCHLORINATED BIPHENYLS EMISSIONS SUMMARY

Test/Compound	Test Date	Sample Volume (DSCM)	Compound Quantity (ng)	Stack Flow Rate (m^3/min)	Concentration (ng/m^3)	Emission Rate (mg/hr)	Emission Rate (µg/kg)
Site A, Test 1*	9/15/81	2,938	--	400	--	--	--
Tri-CBs	--	--	3,380	--	1,150	27.5	5.9
Tetra-CBs	--	--	1,760	--	599	14.3	3.1
Penta-CBs	--	--	70	--	24	0.6	0.1
Hexa-CBs	--	--	15	--	5	0.1	0
Total CBs	--	--	5,225	--	1,178	42.5	9.1
Site A, Test 3	9/22/81	6.814	--	550	--	--	--
Tri-CBs	--	--	350	--	51	1.7	0.4
Tetra-CBs	--	--	510	--	75	2.5	0.5
Penta-CBs	--	--	560	--	82	2.7	0.6
Hexa-CBs	--	--	330	--	48	1.6	0.3
Total CBs	--	--	1,750	--	256	8.5	1.8

*Impinger contents not analyzed.

TABLE 19. ALDEHYDES EMISSIONS SUMMARY

Test/Compound	Test Date	Sample Volume (DSCM)	Compound Quantity (ng)	Stack Flow Rate (m^3/min)	Concentration (ng/m^3)	Emission Rate (mg/hr)	Emission Rate (µg/kg)
Site A, Test 2	9/21/81	4,517	--	652.9	--	--	--
Total Aldehydes	--	--	34,000	--	7,749	303.6	65.5
Site A, Test 3	9/22/81	6,814	--	551.3	--	--	--
Total Aldehydes	--	--	5,700	--	837	27.7	6.0
Site B, Test 1	6/17/82	4.619	--	1,365.7	--	--	--
Total Aldehydes	--	--	1,070	--	232	19.0	2.2
Site B, Test 2	6/17/82	4.536	--	1,402.9	--	--	--
Total Aldehydes	--	--	286	--	63	5.3	0.6
Site B, Test 3	6/18/82	5,062	--	1,259	--	--	--
Total Aldehydes	--	--	252	--	50	3.8	0.4

APPENDIX A

SAMPLE PREPARATION PROCEDURES

The analytical procedures employed to separate the halocarbons of interest from the matrix constituents are described below.

PROCEDURES FOR ADDITION OF INTERNAL STANDARDS AND EXTRACTION OF SAMPLES

Liquid Samples (Impinger Condensate, Probe Rinse, Line Rinses, Solvent Blanks)

Measure the total volume of the liquid sample. Transfer approximately one fourth of the total sample to either a precleaned 125 ml or 250 ml glass bottle equipped with a Teflon-lined cap. Add appropriate quantities of the internal standards ($^{37}Cl_4$-2,3,7,8-TCDD, $^{37}Cl_7$-1,2,3,4,6,7,8-HpCDD, $^{37}Cl_8$-OCDD, D_6-3,3',4,4'-tetrachlorobiphenyl, $^{13}C_{16}$-pentachlorophenol, $^{13}C_6$-hexachlorobenzene) to each sample. Depending upon the type of liquid, proceed as described in the following three steps.

Aqueous Impinger Liquids--

Add 50 ml of hexane to the sample, seal the vessel and agitate (a Burell Wrist-Action shaker was employed) for a period of one hour. Allow the vessel to stand and after the aqueous and organic layers separate completely, transfer the hexane layer to a clean 125 ml glass bottle fitted with a Teflon-lined screw-cap. Repeat the hexane extraction two additional times using a 10 ml aliquot of hexane for each extraction. Combine all hexane extracts. Proceed with Sample Clean-up.

Toluene Wash Samples--

Proceed directly to Sample Clean-up.

Methanol Wash Samples--

Add 20 ml of benzene and 30 ml of 1N H_2SO_4 to the sample, cap the vessel and shake for a period of one hour. Allow the vessel to stand and after the layers completely separate, transfer the upper layer to a clean 125 ml glass bottle equipped with a Teflon-lined cap. Repeat the solvent extraction two additional times using a 10 ml aliquot of benzene for each extraction. Combine all benzene extracts. Proceed with Sample Clean-up.

Solid Samples (XAD-2, Particulates, Filter)

Preclean the Soxhlet extraction apparatus plus a glass extraction thimble containing 1g silica gel and a plug of glass wool by charging the extraction apparatus with benzene and refluxing for a period of two hours. Remove the benzene and retain for assessment of background contamination. Remove the glass wool from the thimble and retain the glass wool for subsequent use. For extraction of the XAD-2 resin, accurately weigh an aliquot corresponding to approximately one-half of the total sample (typically 5-15g), and place this into a precleaned thimble. Insert the cleaned glass wool into the glass thimble in order to hold the resin in place. For extraction of combustion particulates, place an accurately weighed aliquot of particulate into a precleaned extraction thimble. Prior to extraction of these solids add to each sample the appropriate quantities of the internal standards: $^{37}Cl_4$-2,3,7,8-TCDD, $^{37}Cl_7$-1,2,3,4,6,7,8-HpCDD, $^{37}Cl_8$-OCDD, D_6-3,3',4,4'-tetrachlorobiphenyl, $^{13}C_6$-hexachlorobenzene, and $^{13}C_6$-pentachlorophenol. Subsequent to addition of the internal standards, insert the thimble containing the spiked sample into a precleaned Soxhlet extractor, charge the Soxhlet flask with benzene, and extract the sample for a period of 16 hours. After extraction, remove the flask from the extractor and quantitatively transfer the extraction solution to a 250 ml glass bottle equipped with a Teflon-lined cap. Concentrate the extract to approximately 40 ml by passing a stream of dry nitrogen over the sample while heating in a 55° sand bath. Proceed with Sample Clean-up.

PROCEDURES FOR WET CHEMICAL AND ELUTION CHROMATOGRAPHIC CLEAN-UP OF SAMPLE EXTRACTS

The following 12 steps were involved in the wet chemical and elution chromatographic clean-up of the sample extracts.

1. Add 20 ml concentrated H_2SO_4 to the bottle containing the sample extract, cap the vessel and shake for 2 minutes. Allow the mixture to stand and after the aqueous and organic layers separate completely, remove and discard the acid layer.

2. Add 20 ml of doubly distilled water to the bottle containing the sample extract, cap the vessel and shake for 2 minutes. Allow the bottle to stand until the aqueous and organic layers separate, and then transfer the aqueous layer to a clean 60 ml bottle equipped with a Teflon-lined cap (retain the aqueous layer for subsequent analysis for chlorophenols).

3. Add 5 ml of 0.1 N KOH to the organic layer and extract the chlorinated phenols from the sample by shaking the mixture for 10 minutes. Transfer base layer to sample bottle containing water wash from 2.

4. Repeat the base extractions in 3 two more times, combining all base extracts in the one bottle. Reserve the base extracts for acetylation of phenols. Continue with clean-up of organic phase for remaining organic constituents.

5. Using the same procedures as applied in Steps 1 and 2, wash the extract successively with 30 ml portions of concentrated H_2SO_4 and doubly distilled water, in each case discarding the water or acid layer. The acid washing procedure is repeated until the acid layer is virtually colorless. Concentrate to 1 ml under a stream of dry nitrogen in a water bath (55°C).

6. Prepare a glass macro-column, 20 mm OD x 230 mm in length, tapered to 6 mm OD on one end. Pack the column with a plug of silanized glass wool, followed successively by 1.0 g silica, 2.0 g silica containing 33% (w/w) 1M NaOH, and 2.0 g silica. Quantitatively transfer the concentrated extract from Step 5 to the column and elute with 90 ml hexane. Collect the entire eluate and concentrate to a volume of 1 ml in a centrifuge tube, as before.

7. Construct a disposable liquid chromatography mini-column by cutting off a Pyrex 5 ml disposable pipette at the 2.0 ml mark and packing the lower portion of the tube with a small plug of silanized glass wool, followed by one gram of Woelm basic alumina, which has been previously activated for at least 16 hours at 600°C in a muffle furnace, and cooled in a dessicator for 30 minutes just prior to use. Quantitatively transfer the concentrate from Step 6 onto the liquid chromatography column, rinse the centrifuge tube consecutively with two 0.3 ml portions of 3% CH_2Cl_2-in-hexane, and also transfer the rinses to the chromatography column.

8. Elute the column with 7 ml of 3% (v/v) CH_2Cl_2-in-hexane and retain the eluate for PCB and chlorobenzene analyses.

9. Elute the column with 20 ml of 50% (v/v) CH_2Cl_2-in-hexane and retain the eluate for CDDs and CDFs analyses.

10. Concentrate each of the retained fractions to a volume of approximately 1 ml by heating the tubes in a water bath while passing a stream of prepurified N_2 over the solutions, as described above. Quantitatively transfer the concentrated fractions into separate 2 ml micro-reaction vessels. Evaporate the solutions in each of the micro-reaction vessels almost to dryness, using the procedures just mentioned, rinse the walls of each vessel with 0.5 ml CH_2Cl_2, and reconcentrate just to dryness.

11. Approximately 1 hour before gas chromatographic-mass spectrometric (GC-MS) analysis, dilute the residue in each micro-reaction vessel with an appropriate quantity of solvent (depending upon the anticipated quantities of analytes in each vessel) and gently swirl the solvent in the vessel to ensure dissolution of CDDs, CDFs, PCBs, and chlorobenzenes.

12. If preliminary GC-MS screening analysis of the sample indicates the presence of potential interfering compounds (that is, which obscure the CDD, CDF, PCB or other signals of interest), or other sample matrix constituents which elute from the GC at very long times, then additional sample clean-up or fractionation is required using high performance liquid

chromatography (HPLC). The HPLC used for this purpose is described below.* The sample is injected into the HPLC and appropriate fractions, determined in advance by measuring the retention times of pure CDD and CDF standards, are collected.

ACETYLATION OF SAMPLE EXTRACTS FOR CHLOROPHENOL ANALYSIS

The following 10 steps were involved in the acetylation of samples for chlorophenol analyses.

1. Check the pH of the solution with pH paper and add HCl if necessary to adjust the pH to <3.

2. Add 5 ml of benzene to the acidified mixture and agitate the sample for 10 minutes using a wrist-action shaker. Allow to stand for complete layer separation (centrifuge if necessary).

3. Transfer the benzene layer to a 60 ml flint glass bottle (fitted with a Teflon-lined cap) that contains approximately 2 g of anhydrous Na_2SO_4.

4. Repeat step 2 two more times, combining all extracts and then shake the bottle to dry the benzene solution.

5. Transfer approximately 10 ml of the benzene solution into a 16 x 100 mm screw-capped test tube fitted with a Teflon-lined cap.

6. Concentrate the solution in the tube to a volume of approximately 1 ml by passing a stream of purified N_2 over the surface of the liquid, while applying gentle heat (50°C) to the test tube. Add more of the solution and continue to concentrate until all of the solution has been transferred and concentrated.

7. Add 5 ml of benzene to a 60 ml bottle containing Na_2SO_4, shake to rinse the bottle, and transfer the benzene into the test tube containing the previously concentrated solution and concentrate as in Step 6 to approximately 1 ml.

8. Add 2.0 ml isooctane, 2.0 ml acetonitrile, 25 µl pyridine, and 10 µl acetic anhydride to the test tube containing the extract and agitate for 5 minutes on a wrist-action shaker.

9. Add 6 ml of 10 mM H_3PO_4 to the test tube and agitate for 2 minutes on a wrist-action shaker.

10. Remove the organic layer and concentrate it in a Reacti-vial at room temperature (using prepurified N_2) to dryness just before analysis.

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*A Varian Model 5021 Microprocessor Controlled High Performance Liquid Chromatograph equipped with a CDS-111L Data System was employed. Dual Dupont Zorbax ODS Columns (25 cm x 0.6 cm I.D.) were employed. Methanol was employed as the mobile phase in the isocratic mode.

APPENDIX B

DISTRIBUTION OF ORGANIC COMPOUNDS IN THE SAMPLE TRAIN

TABLE B-1. DISTRIBUTION OF CDDs IN SAMPLE TRAIN (%), SITE A, TEST 2

	TCDDs	PCDDs	HxCDDs	HpCDDs	OCDD
Methanol Wash/Front of Sampling Train	<1	1	1	2	3
Particulate Filter, Toluene Wash/Front of Sampling Train	8	9	9	21	41
Impinger Catch	40	37	30	32	21
Methanol Wash/Back of Sampling Train	3	2	2	3	3
Toluene Wash/Back of Sampling Train	33	40	39	29	24
XAD-2 Trap	16	11	19	13	8

TABLE B-2. DISTRIBUTION OF CDDs IN SAMPLE TRAIN (%), SITE A, TEST 3

	TCDDs	PCDDs	HxCDDs	HpCDDs	OCDD
Methanol Wash/Front of Sampling Train	1	1	1	1	3
Particulate Filter, Toluene Wash/Front of Sampling Train	16	21	44	83	82
Impinger Catch	37	36	19	5	3
Methanol Wash/Back of Sampling Train	2	1	1	1	1
Toluene Wash/Back of Sampling Train	24	30	30	8	10
XAD-2 Trap	20	11	5	2	1

TABLE B-3. DISTRIBUTION OF CDDs IN SAMPLE TRAIN (%), SITE B, TEST 1

	TCDDs	PCDDs	HxCDDs	HpCDDs	OCDD
Methanol Wash/Front and Back of Sampling Train	ND	ND	45	33	35
Particulate Filter, Toluene Wash/Front of Sampling Train	100	100	55	33	35
Impinger Catch	ND	ND	ND	5	10
Toluene Wash/Back of Sampling Train	ND	ND	ND	27	18
XAD-2 Trap	ND	ND	ND	2	2

ND = None Detected

TABLE B-4. DISTRIBUTION OF CDDs IN SAMPLE TRAIN (%), SITE B, TEST 3*

	TCDDs	PCDDs	HxCDDs	HpCDDs	OCDD
Methanol Wash/Front and Back of Sampling Train	4	9	9	9	10
Particulate Filter, Toluene Wash/Front of Sampling Train	1	1	3	4	9
Impinger Catch	54	34	43	35	30
Toluene Wash/Back of Sampling Train	36	51	42	49	46
XAD-Trap	5	5	3	3	5

*Composite of Tests 3 and 4

TABLE B-5. DISTRIBUTION OF DCFs IN SAMPLE TRAIN (%), SITE A, TEST 2

	TCDDs	PCDDs	HxCDDs	HpCDDs	OCDD
Methanol Wash/Front of Sampling Train	1	1	1	3	2
Particulate Filter, Toluene Wash/Front of Sampling Train	7	10	8	25	33
Impinger Catch	45	36	33	26	24
Methanol Wash/Back of Sampling Train	3	3	2	4	3
Toluene Wash/Back of Sampling Train	31	40	42	30	26
XAD-2 Trap	13	10	14	12	12

TABLE B-6. DISTRIBUTION OF CDFs IN SAMPLE TRAIN (%), SITE A, TEST 3

	TCDFs	PCDFs	HxCDFs	HpCDFs	OCDF
Methanol Wash/Front of Sampling Train	1	1	1	2	3
Particulate Filter, Toluene Wash/Front of Sampling Train	6	10	21	61	74
Impinger Catch	41	46	30	16	6
Methanol Wash/Back of Sampling Train	3	2	2	1	1
Toluene Wash/Back of Sampling Train	28	31	38	16	13
XAD-2 Trap	21	10	8	4	3

TABLE B-7. DISTRIBUTION OF CDFs IN SAMPLE TRAIN (%), SITE B, TEST 1

	TCDFs	PCDFs	HxCDFs	HpCDFs	OCDF
Methanol Wash/Front and Back of Sampling Train	1	ND	50	50	42
Particulate Filter, Toluene Wash/Front of Sampling Train	99	100	50	50	42
Impinger Catch	ND	ND	ND	ND	7
Toluene Wash/Back of Sampling Train	ND	ND	ND	ND	9
XAD-2	ND	ND	ND	ND	ND

ND = None Detected

TABLE B-8. DISTRIBUTION OF CDFs IN SAMPLE TRAIN (%), SITE B, TEST 3*

	TCDFs	PCDFs	HxCDFs	HpCDFs	OCDF
Methanol Wash/Front and Back of Sampling Train	6	7	5	3	4
Particulate Filter, Toluene Wash/Front of Sampling Train	1	1	4	2	6
Impinger Catch	24	27	34	34	32
Toluene Wash/Back of Sampling Train	59	61	52	60	55
XAD-2 Trap	10	4	5	1	3

*Composite of Tests 3 and 4

TABLE B-9. DISTRIBUTION OF ClBs IN SAMPLE TRAIN (%), SITE A, TEST 2

	DClBs	TrClBs	TeClBs	P5ClBs	HxClB
Methanol Wash/Front of Sampling Train	4	2	1	1	1
Particulate Filter, Toluene Wash/Front of Sampling Train	2	3	13	7	6
Impinger Catch	ND	27	22	77	15
Methanol Wash/Back of Sampling Train	1	<1	1	<1	2
Toluene Wash/Back of Sampling Train	45	3	9	3	8
XAD-2 Trap	48	65	54	12	68

ND = None Detected

TABLE B-10. DISTRIBUTION OF ClBs IN SAMPLE TRAIN (%), SITE A, TEST 3

	DClBs	TrClBs	TeClBs	P5ClBs	HxClB
Methanol Wash/Front of Sampling Train	ND	<1	<1	<1	<1
Particulate Filter, Toluene Wash/Front of Sampling Train	ND	1	2	2	4
Impinger Catch	ND	<1	<1	1	2
Methanol Wash/Back of Sampling Train	ND	ND	ND	ND	ND
Toluene Wash/Back of Sampling Train	ND	ND	ND	<1	1
XAD-2 Trap	100	99	98	97	93

ND = None Detected

TABLE B-11. DISTRIBUTION OF ClBs in Sample Train (%), Site B, Test 1

	DClBs	TrClBs	TeClBs	P5ClBs	HxClB
Methanol Wash/Front and Back of Sampling Train	ND	ND	ND	ND	57
Particulate Filter, Toluene Wash/Front of Sampling Train	ND	ND	3	ND	43
Impinger Catch	50	27	44	ND	ND
Toluene Wash/Back of Sampling Train	ND	19	38	ND	ND
XAD-2 Trap	50	54	15	ND	ND

ND = None Detected

TABLE B-12. DISTRIBUTION OF ClBs IN SAMPLE TRAIN (%), SITE B, TEST 3*

	DClBs	TrClBs	TeClBs	P5ClBs	HxClB
Methanol Wash/Front and Back of Sampling Train	ND	ND	ND	32	19
Particulate Filter, Toluene Wash/Front of Sampling Train	ND	ND	21	ND	7
Impinger Catch	ND	ND	ND	ND	ND
Toluene Wash/Back of Sampling Train	ND	ND	ND	30	65
XAD-2 Trap	100	100	79	38	9

*Composite of Tests 3 and 4
ND = None Detected

TABLE B-13. DISTRIBUTION OF CPs IN SAMPLE TRAIN (%), SITE A, TEST 2

	TrCPs	TeCPs	P5CP
Methanol Wash/Front of Sampling Train	ND	ND	ND
Particulate Filter, Toluene Wash/Front of Sampling Train	2	2	3
Impinger Catch	46	48	51
Methanol Wash/Back of Sampling Train	<1	<1	ND
Toluene Wash/Back of Sampling Train	3	7	20
XAD-2 Trap	49	43	26

ND = None Detected

TABLE B-13. DISTRIBUTION OF CPs IN SAMPLE TRAIN (%), SITE A, TEST 2

	TrCPs	TeCPs	P5CP
Methanol Wash/Front of Sampling Train	ND	ND	ND
Particulate Filter, Toluene Wash/Front of Sampling Train	2	2	3
Impinger Catch	46	48	51
Methanol Wash/Back of Sampling Train	<1	<1	ND
Toluene Wash/Back of Sampling Train	3	7	20
XAD-2 Trap	49	43	26

ND = None Detected

TABLE B-14. DISTRIBUTION OF CPs IN SAMPLE TRAIN (%), SITE A, TEST 3

	TrCPs	TeCPs	P5CP
Methanol Wash/Front of Sampling Train	ND	ND	ND
Particulate Filter, Toluene Wash/Front of Sampling Train	2	2	4
Impinger Catch	78	85	82
Methanol Wash/Back of Sampling Train	<1	<1	ND
Toluene Wash/Back of Sampling Train	1	2	7
XAD-2 Trap	19	11	7

ND = None Detected

TABLE B-15. DISTRIBUTION OF CPs IN SAMPLE TRAIN (%), SITE B, TEST 1

	TrCPs	TeCPs	P5CP
Methanol Wash/Front and Back of Sampling Train	<1	2	20
Particulate Filter, Toluene Wash/Front of Sampling Train	<1	2	16
Impinger Catch	11	17	19
Toluene Wash/Back of Sampling Train	53	59	32
XAD-2 Trap	36	20	13

TABLE B-16. DISTRIBUTION OF CPs IN SAMPLE TRAIN (%), SITE B, TEST 3*

	TrCPs	TeCPs	P5CP
Methanol Wash/Front and Back of Sampling Train	13	29	71
Particulate Filter, Toluene Wash/Front of Sampling Train	1	1	3
Impinger Catch	24	40	16
Toluene Wash/Back of Sampling Train	11	14	6
XAD-2 Trap	51	16	4

*Composite of Tests 3 and 4

TABLE B-17. DISTRIBUTION OF PCBs IN SAMPLE TRAIN (%), SITE A, TEST 3

	TrCBs	TeCBs	P5CBs	HxCBs
Methanol Wash/Front of Sampling Train	ND	ND	ND	ND
Particulate Filter, Toluene Wash/Front of Sampling Train	20	20	20	ND
Impinger Catch	12	24	39	55
Methanol Wash/Back of Sampling Train	ND	ND	ND	ND
Toluene Wash/Back of Sampling Train	11	25	27	36
XAD-2 Trap	57	31	14	9

ND = None Detected

APPENDIX C

QUALITY ASSURANCE AND CONTROL

The data collected and reported by Scott from emissions test projects are verified through an on-going Quality Assurance/Quality Control (QA/QC) program. This can be divided into three types of procedures depending on the method of testing. These three categories of test procedures are:

Physical Test Methods
Chemical Test Methods
Instrumental Test Methods

The third category which involves continuous emissions monitoring was not a part of this test program.

Physical test methods include pressure, temperature and flow measurements of liquid and gaseous process streams and gravimetric sampling procedures including isokinetic particulate testing. Each piece of equipment used to produce a quantitative value is subjected to a scheduled calibration program. A typical interval is every six months. The equipment is marked in such a way that it can be individually identified; and a log is kept on its calibration history. Examples of equipment so calibrated are thermocouple bridges, magnehelic pressure gauges, pitot tubes, gas meters, orifices and sampling nozzles. The orifices and gas meters in Scott's meter boxes are calibrated separately and then as a unit. The standard used is a reference test meter calibrated against a spirometer. Scott maintains a wind tunnel for pitot tube and velocimeter calibrations. In addition, Scott participates in EPA's audit sample program for meter box calibration. The results of these audits have demonstrated the accuracy and consistency of our measurement techniques and the results of an excellent equipment maintenance program. Scott's analytical balance is regularly maintained by the Mettler Company.

Chemical analysis involved analysis of collected samples for HCl content by titration procedures and for chlorinated organic compounds and aldehydes by GC/MS and HPLC. QA/QC procedures included analysis of solvent and method blanks as well as certified standards. Titrations and injections were also performed in duplicate or as often as necessary to receive duplication to within ±10%. Furthermore, quality control for the individual organic compound analysis was provided on a continuing basis by the incorporation of known quantities of stable-isotopically labelled internal standards into each sample prior to analysis.

QA/QC procedures for calculations and report writing were based on a system of internal reviews. All calculations were double checked as were the basic procedures and assumptions used in performing the calculations. The final report was prepared under the supervision and guidance of the Project Manager. In addition, the Vice President and General Manager of Scott's Environmental Services Division maintained a constant awareness of the project proceedings and reviewed the final report prior to issuance.

GLOSSARY

class of Compounds: Identification of a group of compounds by degree of chlorination, e.g. monochloro, dichloro, etc.

isomer: One of two or more molecules having the same number and kind of atoms and hence the same molecular weight, but differing with respect to the arrangement or configuration of the atoms.

monochlor: Prefix for a molecule containing one Cl atom.

dichlor: Prefix for a molecule containing two Cl atoms.

trichlor: Prefix for a molecule containing three Cl atoms

tetrachlor: Prefix for a molecule containing four Cl atoms.

pentachlor: Prefix for a molecule containing five Cl atoms.

hexachlor: Prefix for a molecule containing six Cl atoms.

heptachlor: Prefix for a molecule containing seven Cl atoms.

octachlor: Prefix for a molecule containing eight Cl atoms.

nonachlor: Prefix for a molecule containing nine Cl atoms.

decachlor: Prefix for a molecule containing ten Cl atoms